DYEING SILK,
MIXED SILK FABRICS
AND ARTIFICIAL SILKS

DR. A. GANDSWINDT

LIBRARY

SOUTHEASTERN MASSACHUSETTS UNIVERSITY · UNITATE · 1895 · FORTIOR

$9^{\underline{50}}$

57

DYEING
SILK, MIXED SILK FABRICS
AND ARTIFICIAL SILKS

Digitized by the Internet Archive
in 2010 with funding from
Boston Library Consortium Member Libraries

http://www.archive.org/details/dyeingsilkmixeds0gans

DYEING SILK, MIXED SILK FABRICS AND ARTIFICIAL SILKS

BY

DR. A. GANSWINDT

TRANSLATED FROM THE GERMAN BY

CHARLES SALTER

LONDON
SCOTT, GREENWOOD & SON
8 BROADWAY, LUDGATE, E.C.4
1921

[*The sole rights of translation into English remain with Scott, Greenwood & Son.*]

Printed in Great Britain by
Richard Clay & Sons, Limited,
Paris Garden, Stamford St., S.E. 1,
and Bungay, Suffolk.

NB 2861

TP90
G3

S.M.T.I. LIBRARY

PREFACE

THERE is no lack of works on Dyeing in general, but unless they are extremely voluminous and expensive, they cannot treat the different branches of the industry with the desired thoroughness. Consequently, the practical man, wherever this is possible, turns to a special work in which he can find sufficient information on all the requisite details of his particular subject.

Such works specially devoted to the dyeing of silk are rare, and it is to fill this gap that the present book has been written. Based on a practice of more than twenty years as a teacher, and the experience gained thereby, the author has treated all the material dealing with this special branch in a readily comprehensive manner, and thus placed in the hands of the silk dyer a book that will be useful.

THE AUTHOR.

CONTENTS

PAGE

INTRODUCTION 1

CHAPTER I

SILK 4
- Further Treatment of Raw Silk 5
- Scouring 6
- Souple, or Half-scoured Silk 9
- Écru, or Hard Silk 12
- Sundry Operations Preceding Dyeing 12
- Bleaching Silk 14
- Loading 18
- Physical and Chemical Properties of Silk . . . 30
- Estimating the Value of Silk 38
- Mechanical Operations in Silk Dyeing 39
- Dyeing Machinery and Appliances 41
- Water in Silk Dyeing 43
- Chemicals Used in Silk Dyeing 49
  - Acids 49
  - Bases 52
  - Salts 52
  - Soaps 60
  - Sundries 62
- Mordanting Silk 63
- Bast Soap: Its Properties, Application and Action . 68
- Behaviour of Silk Towards Dyestuffs 72
- Selecting the Dyestuffs and Preparing the Baths . 76
- Dyeing with Basic Dyestuffs 80
- Dyeing with Acid Dyestuffs 85
- Dyeing with Substantive Dyestuffs 94
- Dyeing with Diazotised Dyestuffs 98
- Dyeing with Sulphone Dyestuffs 102

SILK (*continued*) PAGE
Dyeing with Mordant Dyestuffs 102
Dyeing with Sulphur Dyestuffs 108
Dyeing with Vat Dyestuffs 110
Dyeing with Natural Dyestuffs 115
Black-dyeing Silk 117
Testing Dyed Silk for Loading 133
Colour-dyeing 136
Dyeing Chappe Silk 144
Special Effects in Silk Dyeing 146
Dyeing Silk in the Piece 148
Matching 149
Testing Silk-dyeings for Fastness 151
Treatment of Silk after Dyeing 154
Gilding Silk 157

CHAPTER II

TUSSAH 158
Scouring, Bleaching and Loading Tussah . . . 161
Dyeing Tussah 165

CHAPTER III

WOOL-SILK 170
Wool-Silk and its Treatment Before Dyeing . . . 170
Dyeing Wool-Silk 177
Dichroic Effects on Wool-Silk 182

CHAPTER IV

HALF-SILK FABRICS 186
Half-Silk Fabrics and Their Preparatory Treatment . 186
Properties of Half-silk and its Behaviour Towards Dyestuffs 188
Dyeing Half-Silk 193
Dichroic Effects on Half-Silk 200
Black on Half-Silk 201
Dyeing Silk-Wool-Cotton Fabrics 204
Mechanical Operations in Half-Silk Dyeing . . . 205

CHAPTER V

PAGE
Artificial Silk 207
Commercial Grades of Artificial Silk and Their Properties 207
Dyeing Artificial Silk 209
Fabrics with Fancy Threads of Artificial Silk . . 212

Index 215

DYEING SILK

INTRODUCTION

In dealing with the subject of dyeing silk, it is advisable, in the first place, to have a clear understanding of what is meant by the term "silk." It is true that the term is, or at least was, so closely circumscribed that a new definition would seem unnecessary; but during the last twenty-five years a large number of articles, all claiming to be "silk," have come on the market, and there are now so many varieties of silks that it takes an expert to "divide the sheep from the goats." The layman and the beginner will find great difficulty in finding their way through this wilderness of "silks," as may be gathered from the following list: waste silk, acetate silk, ailanthus silk, bast silk, bourette silk, chappe silk, Chardonnet silk, cocoon silk, collodion silk, corah silk, cordonnet silk, cuite silk, écru silk, Fagara silk, flock silk, florette silk, lustre silk, grége silk, half-silk, artificial silk, Lehner silk, Linkmeyer silk, marabout silk, mulberry silk, mussel silk, organzine silk, Pauly silk, down silk, raw silk, simili silk, souple silk, hank silk, trame silk, Tussah silk, viscose silk, Vivier silk, wild silk, wool-silk, Yamamai silk, and numerous others.

In the above list, the natural and artificial silks are given indiscriminately, with the intention of showing how necessary a new definition of the term "silk" has become. In the present work the name will be restricted, as a matter of principle, to natural silks, excluding all the artificial kinds entirely. Moreover, among the numerous natural varieties, only those textile fibres will be considered " silk " as are spun by the true silkworm, *Bombyx mori*, in making its cocoons. This natural variety is also known as " mulberry silk," and is the handsomest, finest, and therefore the most highly valued of all the natural silks. At the same time it forms the foundation of the silkworm industry. The silkworm can be cultivated, whereas, with few exceptions, all the other larvæ that are capable of spinning a silken thread and building a cocoon can only be cultivated with difficulty, if at all—at least, none of the attempts hitherto made in this direction has led to any really satisfactory result. All the natural silks spun by larvæ which cannot be cultivated, or only with difficulty, will be classed as " wild silks," the best known representative of which is the Tussah silk met with in commerce as a fabric, and also—under the name " bast silk "—in hank form. The present work will deal with the dyeing of Tussah as well as true silk.

Mussel or Byssus silk is a natural textile fibre, not spun by a worm, but secreted by the Byssus gland in certain mussels (*e. g.* Pinna). In both physical and chemical properties it differs considerably from true silk, and cannot therefore really be classed as a silk. Moreover, it is of merely subsidiary importance.

The case is quite different, however, with artificial silk, which, in the course of years, has become such an important article of commerce that it cannot be ignored here. As a matter of fact, the name " artificial silk " is not happily chosen, since the article is not a silk prepared by artificial means. True, it is an artificial product, but no silk; being an artificial textile fibre prepared by a complicated process, and exhibiting an excellent lustre which is even not inconsiderably superior to that of true silk. In every other respect, however, the artificial silks of commerce (for there are numerous varieties) have nothing in common with natural silk but the name—and that wrongly, because natural silk is a product of animal vitality, whereas all artificial silks are of vegetable origin. Consequently, these latter can only replace natural silk in so far as their characteristic silky lustre is concerned, there being no comparison between the two in respect of tensile strength and fineness. Nevertheless, the artificial silks have acquired a sphere of usefulness, quite independent of that of natural silk, and they will therefore be dealt with, in a special supplementary chapter, though not as "silk."

Wool-silk is a term for fabrics made of silk and wool, in some of which (such as "Gloria" fabrics) both fibres are of equal importance, whereas in others the silk appears as decorative designs (flowers or stripes) or threads. Wool-silk therefore belongs to the class of mixed fabrics.

Half-silk is a name for fabrics of silk and cotton woven together in such a manner that the silk forms the face and the cotton the wrong side of the material.

Fabrics containing silk, wool and cotton at the same time will also be taken under consideration.

CHAPTER I

SILK

ONLY a brief summary need be given of the method of producing silk. The silkworm undergoes the pupal change and spins an enveloping cocoon, and after a short time the pupa is killed by treating the cocoon with hot steam. The cocoon is nothing more than a thread of raw silk, about 400 to 1300 yds. in length, weighing only about 4 grains and wound to form an oval envelope, from which it is unwound, in lukewarm water, by means of a reel. The extreme outer and inner layers of the cocoon thread are inferior, and are discarded as waste silk. In reeling, the silk is also graded according to quality. The best cocoons are worked up into organzine, which is used exclusively for warp threads. The second quality is destined to become trame silk, or weft. Cocoons that are considered as not worth reeling, and also the aforesaid outer ends of the cocoon filament and the agglutinated interior of the cocoon, in immediate contact with the pupa, furnish the material for the production of chappe and florette silk, whilst the remaining waste forms bourette silk. The extreme outer ends of the cocoon filament are also termed " flock " silk.

The filament obtained from the cocoon by reeling is raw silk, or *grége*. The length of raw silk filament yielded by normal cocoons ranges from 300 to 1000 yds. Raw silk is not at all the handsome, lustrous, soft and supple thread that one is accustomed to speak of as " silk," but a somewhat unsightly, hard, round, smooth and uniform filament, not unlike a thin violin string. In addition to the actual silk fibre, it contains the whole of the bast in which the latter is enclosed and with which the larva gums the individual delicate silk filaments together in spinning the cocoons. There is no need to go into the details of the operation of reeling, as these are fully described in existing works on silk, together with the subsequent processes of doubling, twisting, etc. Organzine and trame are chiefly used for weaving silk fabrics, whilst chappe is mainly employed in the manufacture of plush and velvet.

Further Treatment of Raw Silk

Consideration of the complex nature of raw silk leads one logically to inquire how the crude article is transformed into one possessing the valuable properties of pure silk. It has already been stated that the raw silk is composed of two entirely different constituents: the actual silk fibre (fibroin) and the gum (sericin). The next step, therefore, is to separate these two constituents; and this is a matter presenting no difficulty. The fibroin is insoluble in water, whereas sericin dissolves more or less completely in hot water, and is entirely dissolved in presence of a weak alkali such as soap. On this divergent behaviour of the two constituents is based the operation of scouring or de-gumming the raw silk. The mean relative proportions of the sericin and fibroin are as 1 : 3, *i. e.* raw silk consists of about 25–30% of sericin and 75–70 % of fibroin, some kinds containing as little as 20 % of the former. According to the proportion of sericin removed by scouring, three different qualities of silk are obtained, all of which are known by their French names because the silk industry at one time was carried on almost exclusively in the Lyons district. If the whole of the sericin is removed, only the pure silk fibre being left, the product is known as "cuite" silk (*i. e.* fully boiled-off). When the process is carried on only so far as to reduce the original 25–30 % of sericin to 8–12 %, "souple" silk is obtained (soft, or no longer so hard as raw silk). By controlling the boiling process so that the loss of sericin is kept down to 1–4 %, "écru" raw silk is produced. Whilst raw and écru silk are not actually identical, the difference in sericin content is so slight that the term "écru" is generally extended to cover raw silk as well.

The following classification is based on the sericin content of the silk—

Raw silk, with 25–30 % of sericin.

Écru (hard silk), with 24–26 % of sericin (or 1–4 % loss of sericin).

Souple (soft), with 17–18 % of sericin (loss, 8–10 %).

Cuite (pure silk), with 0 % of sericin (loss, 25–30 %).

SCOURING[1]

As already stated, the sericin of silk is almost or quite completely soluble in water, according to the kind of silk under treatment; and this sericin must be removed by boiling the raw silk. As a matter of fact, however, it is preferred not to resort to actual ebullition, but to work at 90–95° C. in presence of a small quantity of soap, because the sericin dissolves more readily in a weak alkali (water glass, borax), and soap is the solvent generally used. It being necessary to free the scoured silk from the solution of soap and sericin afterwards, only such soaps (*e. g.* Marseilles soap, or soft soap) as are easily washed out should be used. The water must also be free from lime (soft), or lime soaps, difficult to wash out, will be formed. Consequently, hard water must be softened before use.

---

[1] The term "de-gumming," or "removing the bast," is not correct, since raw silk does not possess any bast or rind, or any gum. On the other hand, it contains sericin, or silk gelatin, and the operation would be more accurately termed "de-gelatination."

Technically, the scouring process is carried out in two stages, in hot soap baths. In the first stage, the raw silk is suspended, on smooth pins, in a copper pan or wooden vat, for one and a quarter to two hours, in a bath liquor containing 30–35 % of Marseilles soap at a temperature of 90–95° C. Actual ebullition must be avoided in order to prevent the silk from getting tangled by the violent movement of the water, and also to keep the silk from being stained by the peculiar yellow colouring matter of the sericin. In this bath, the sericin swells up and begins slowly to dissolve; and it is found that only about 15–18 %, or at most 20 %, passes into solution, from which circumstance it may be concluded that sericin consists of two constituents of different solubility. The raw silk from the first bath is only half scoured, and is therefore termed "mi-cuite." Frequently, only a single scouring bath is used, though many silk dyers employ a second, and even a third.

The treatment in the second soap bath is intended to remove the final traces of sericin and obtain maximum softness and flexibility. The old practice was to place the partially scoured silk in hempen bags and boil it for 30 minutes to 3 hours in open copper pans containing a weak solution of soap (10–15 parts of soap per 100 of silk). For dark shades, the boiling-off was conducted in the old scouring bath, strengthened with more soap; but for light shades and white a fresh soap bath was prepared. Nowadays the hanks of silk are suspended on wooden pins and worked about in the bath, by which means the final traces of sericin can be extracted without boiling; and, in fact, there is no evidence to show that actual boiling is essential for obtaining a high degree of flexibility and lustre in the product. In the south of France and in Switzerland it is customary to enter the boiled-off silk in a bath of carbonate of soda, followed by rinsing in water and drying. The soap liquor from the boiling-off bath can be used for scouring.

In a recent manual of instructions to dyers, the Badische Anilin and Soda fabric gives the following recipe for scouring 100 parts of raw silk: Enter the silk in a bath of 4000–6000 parts (by weight) of water (softened, if necessary, with 3–4 parts of carbonate of soda) and 30 parts of Marseilles soap, at a temperature of about 95° C., for three-quarters to one and a half hours, working it about once or twice during that period. Then, if necessary, treat it for another three-quarters of an hour in a second bath, containing half the above quantity of soap, also at about 95° C. Rinse in softened, lukewarm water, wash in cold water and drain in the hydroextractor or wringer. ("Boiling" is not mentioned at all.)

The spent first scouring-bath is a solution of sericin in Marseilles soap, and though not used again for scouring, finds extensive employment (as "bast soap") in silk dyeing. It should, however, be borne in mind that this bast soap will only keep for a short time, and oftentimes begins to decompose in a few days, a condition revealed by the offensive, putrescent smell. Sericin, being a substance of the protein group, is therefore liable to putrefaction, which is also accelerated by the alkali present.

According to Steinbeck, thrown silk is first treated for an hour in a 1–15 % solution of soda crystals at about 90° C., and is then boiled-off with 4–15 % of soap.

For scouring chappe ("spun") silk, the Badische Co. gives the following instructions: Boil the silk (100 parts) for three-quarters of an hour in a bath of 4000–5000 parts of water containing 0·1 % of calcined soda or 0·2 of crystals, working the silk about carefully and not too often. Then enter in a second warm bath, containing 15 parts of Marseilles soap, for three-quarters of an hour, rinse thoroughly and drain in the hydro-extractor or wind off.

Under the foregoing treatment the silk becomes shorter by contraction, and therefore has to be stretched to restore the original length. In some cases, stretching is practised after the first scouring-bath. The operation is carefully performed by hand, on a wringing-post. In this way the length of the fibre is increased by about 3 %, and at the same time the lustre is increased.

Latterly, successful attempts have been made to apply the method of froth dyeing to the scouring of silk, and the process has been patented (Ger. Pat. 179229) by Gebr. Schmidt of Basle. It was originally intended for Tussah silk, sodium perborate being added as a preliminary bleach; but—with omission of the perborate—it has also been used, in many cases, for scouring true silk.

Bourette (waste silk) is not usually scoured, but is dyed without any preliminary treatment.

SOUPLE, OR HALF-SCOURED SILK

Souple, or soft, silk is only partially scoured, about 17–18 % of the 25–30 % of the sericin originally present in the raw silk being removed. The commercial article therefore consists of about 77 % of fibroin and 23–25·3 % of sericin.

The soupling process is divided into two stages, viz.

soaking and softening, a preliminary bleaching being sometimes given in between. Trame silk is the only grade converted into souple, which may be regarded as a raw silk which has only been deprived of just enough of the sericin to remove the feeling of hardness. The average amount of sericin removed is 8 %, but there is no definite standard, and the statements of various authors differ considerably, ranging from 4 to 10 %.

The soaking-bath contains about 10–30 % of Marseilles soap, and the raw silk is entered for about half to one hour, with a bath temperature of 35–40° C. The object of this treatment is to soak the silk thoroughly. The final effect varies, naturally, according to the strength and temperature of the bath and the period of immersion, and consequently there is no check on the varying statements as to the loss of sericin sustained, only a portion of this constituent being extracted from the fibre in this bath. After the operation the silk is wound off and the soap is removed by a thorough rinsing.

For the preliminary bleaching treatment, either aqua regia or sulphuring is employed. The process will be described later, when dealing with the bleaching of silk. Of course, where the souple silk is intended for medium or dark shades, this stage may be omitted.

The second stage consists in treating the silk in a weak acid bath, cream of tartar being mostly used, though equally good results can be obtained with sulphurous acid or very dilute hydrochloric acid. The object of the treatment is to convert the residual sericin on the fibre into a less readily soluble form, so that it can no longer be dissolved away in the subsequent process of dyeing.

A number of recipes have been given for the soupling bath, all of them being more or less capable of producing the desired result, provided boiling is avoided, since it would thwart the purpose in view by causing a further loss of sericin. The Badische Co. recommends, for 100 parts of raw silk, a bath (temperature 80–90° C.) containing 4 parts of cream of tartar, 10 parts of commercial sulphuric acid, or 15 parts of aqueous sulphurous acid, according to the kind of silk, the bast, and the subsequent treatment in view. Bayer & Co. advise treating at 65–90° C. in a bath containing 8–10 % of cream of tartar, 1 % of commercial sulphuric acid, and 10% of sulphurous acid. Steinbeck prescribes a bath of 10 % of commercial sulphuric acid, ½ % of sulphurous acid and 2 % of sulphate of magnesia, at a temperature of 75° C.; whereas Silbermann recommends 1 part of sulphate of magnesia and 0·25 of sulphuric acid to 85 parts of silk. Ganswindt prefers a 0·4 % solution of cream of tartar, and Dumont a bath containing 3 % of hydrochloric acid and 4 % of alcohol. Other soupling agents that have been proposed include: sodium bisulphate; sodium bisulphite; sulphuric acid and soap, and the same acid in conjunction with cream of tartar. Silbermann also speaks of using a boiling-hot solution of soap; but this can hardly be accurate, because it would result in the production of cuite, or fully scoured silk, and not souple. That treatment in weak acid baths induces a morphological change in sericin is also evident from the fact that souple silk is more voluminous than raw silk, and being plumper produces the impression of a full, heavy thread, such as is required for weft. However, although it seems to form a plump, very strong, thick, heavy thread, souple is really an inferior material, as is clearly evident from its dull sheen. Nevertheless, it enjoys considerable popularity, more particularly because the sericin it contains is able to take up large quantities of loading ingredients readily, so that it can be loaded far more extensively than

S.M.T.I. LIBRARY

pure silk, and is, moreover, generally dyed in the loaded condition.

After this semi-scouring process, which may take from 2 to 5 hours according to the quality of the silk and the method adopted, the souple is neutralised, preferably by rinsing it once in hot water and twice in cold. Owing to the presence of the not inconsiderable amount of sericin it still contains, it must not subsequently be treated in hot soap-baths or in warm baths of dilute alkali, though it will stand boiling acid-baths, the sericin being less soluble in weak acids than in pure water. On this account, souple silk is better dyed at lower temperatures than are used for pure silk.

Experience having shown that each silk behaves differently, and that the sericin behaves in accordance with the kind of silk, no general rules can be laid down, so many factors coming into operation. Soupling, therefore, requires great experience, and thus belongs to the most difficult processes in silk dyeing.

Écru, or Hard Silk

Écru or Crue is prepared from raw silk by soaking in lukewarm water (or preferably in soap solution) and then rinsing. Under this treatment, the silk loses 1–5 % of sericin, according to the duration of the process. For white and pale shades it is bleached, but in the main it is used for blacks (velvet weft). Écru is also employed for veiling.

Sundry Operations Preceding Dyeing

In all cases where the production of medium or dark shades is in question, the various kinds of silk mentioned in the foregoing require no intermediate treatment before dyeing. If, however, pure white silk is required, or the production of pale, delicate shades is in question, the silk must be bleached.

The object of bleaching is the complete destruction of the natural colouring matters of the silk; and since this object can be achieved both by oxidation and by reduction, there are two classes of methods and agents which can be employed. Speaking generally, oxidation bleaching processes offer a better guarantee for the complete destruction of the natural colouring substances in the silk. The actual method to be selected in any individual instance will depend primarily on the quality of the particular silk and the practical requirements the bleached silk is expected to fulfil. These will be dealt with in the section relating to bleaching.

In all circumstances the operations of scouring and softening cause a loss of weight in the raw silk. This is in accordance with the nature of things, and, to the logical thinker, quite in order; but to the silk manufacturer this inevitable decrease in weight constitutes a loss which calls for replacement. To meet this call, which is difficult to excuse, and is, at heart, absurd, recourse is had to the objectionable practice of loading the silk, a disreputable industry whose final object is deliberate deception of the purchasing public. This ill-starred practice of loading is a cancer in the silk industry, and is recognised as such in the industry itself; but, although attempts have not been lacking to combat the evil, or at least keep it within moderate bounds, it has proved ineradicable and must be reckoned with as unavoidable. In order to make good the loss in weight resulting from scouring and softening, substances are incorporated with the scoured or souple silk which, although not themselves silk, are intended to compensate the manufacturer for the perfectly natural decrease in weight sustained by that material. At first, loading was conducted on a modest scale, and manufacturers were content to restore the lost weight to par: silk which originally consisted, for example, of 75 % of fibroin and 25 % of sericin, having the latter replaced by 25 % of loading ingredients. Now, however, there are silks in the market which are loaded to 300 or 400 % above par; that is to say, contain 325 to 425 parts of loading ingredients to 75 parts of silk substance. In other words, such a silk consists of 19–15 % of silk fibre and 81–85 % of loading, so that cannot really lay any claim to be called "silk." Moreover, since not only cuite silk is loaded, but also (and preferably) souple —which has lost not more than about 8 % in weight— the existence of souple silks loaded up to 800 and 900 % indicates unscrupulous profiteering. It constitutes a partially legalised fraud, which is carried on openly and as a matter of general knowledge, the apology put forward to cloak it being a desire to place cheap silk goods on the market. Whilst it is true that this class of silks is apparently cheap, the goods are in reality far too dear if their actual value in silk be taken into account. The subject is dealt with a little further on.

BLEACHING SILK

1. *Bleaching Cuite Silk.*—Pure silk is bleached by sulphuring exclusively, the method described below being repeated up to four times, according to the degree of whiteness required. The scoured silk from the final scouring bath is passed through 4–5 faintly alkaline rinsing baths and then entered direct into the sulphuring chamber. Wherever possible, the palest threads are selected for white silk; but if none but those with yellow bast are available, sulphuring alone is not sufficient and hydrogen peroxide must be used for bleaching. Thrown silk and chappe

(spun silk) also must be bleached with hydrogen peroxide, or, better still, with sodium peroxide.

2. *Bleaching Souple Silk.*—In this case the bleaching usually precedes the soupling process, yellow raw silk being treated with aqua regia, and white with gaseous sulphurous acid, or, more rarely, with a bath containing aqueous sulphurous acid and sulphuric acid. Aqua regia turns the yellow silk a greenish shade, the material being worked about in the bath until this coloration appears. The greenish shade is perfectly normal, and disappears after sufficient rinsing. The appearance of a yellow tinge in the green indicates that the operation has been carried too far, and the silk will then be unsuitable for dyeing light shades. White souples are also sulphured again after the softening process.

3. *Bleaching Hard* (*Écru*) *Silk.*—The object of bleaching here is to destroy the natural colouring matters without injuring the bast in the slightest degree. Here again, sulphuring is the usual treatment; but the other methods described below may also be employed.

For the sulphuring process, the damp silk is exposed to the action of sulphur fumes for 24–36 hours in one or more sulphuring chambers or boxes in succession. The arrangement of the apparatus may be assumed to be known. Dry silk will not bleach at all, and as even the damp material bleaches but slowly, the operation must be repeated according to requirements. The process is followed by a thorough washing in soft water. The bleaching fumes are produced by burning fragments of stick sulphur in boxes.

If aqueous sulphuric acid is to be used, a bath is prepared by gradually stirring 1 volume of sulphuric acid (60% Bé.) into 10 volumes of sulphurous acid. The silk is worked about energetically in the cold liquor. When bleaching is completed, the silk is first treated in a cold solution of carbonate of soda and then with warm soap solution. The sulphuring is repeated according to requirements.

In all cases, no matter whether gaseous or aqueous sulphurous acid be used, it is essential that the sulphuring should be immediately followed by warm rinsing. Although a recognised reducing agent, sulphurous acid acts in a different manner in this process, combining with the natural colouring matter to form a soluble, but unstable, leuco compound, which must be separated from the silk as quickly and completely as possible. Hence, stress must be laid on a thorough rinsing with soft water, otherwise the bleaching effect will be merely temporary, because if the sulphite compound be left in the silk it will decompose, rapidly by subsequent contact with acids and more slowly by the action of atmospheric carbon dioxide. In this way the original colouring matter will be reconstituted and—solely as the result of insufficient washing—the bleached silk will revert to its primitive colour. After neutralising, it is desirable to enter the silk in a weak soap bath, and to blue it if considered necessary.

A more powerful agent is sodium hydrosulphite, which is the substance used in preparing the hydrosulphite bath, and is obtainable in commerce with a density of 17° Bé. For bleaching, it is diluted to 3° Bé. and mixed with about 1 % of acetic acid, the silk being entered at once. The operation takes about 6 hours, and the goods should then be lightly rinsed.

A method frequently used, and one that is much simpler to carry out, is bleaching with aqua regia, which is generally employed for producing bleached souple silk from yellow raw silk, the bleaching preceding the softening process. The bath mixture consists of 1 part of nitric acid and 5 of hydrochloric acid, made up to a strength of 25° Bé. and then left for 4–5 days, being diluted to about 3° Bé. for use. The silk is worked about in the bath for a quarter of an hour, at 20–35° C., and is at once thoroughly washed and sulphured. According to Silbermann, on the other hand, equal parts of hydrochloric acid (sp. gr. 1·18) and nitric acid (sp. gr. 1·334) should be left to stand for several days at 35° C., and finally diluted to 3–4° Bé. The Badische Co. prescribes 3 parts of hydrochloric acid to 1 of nitric acid, with dilution to 3° Bé. Varying statements are made as to the quantity of bath liquor required. As the silk is worked about it turns dark green and then a greenish grey. The process should be completed by sulphuring. The manner in which the nitrosyl chloride—the active ingredient of aqua regia—acts in this case has not yet been fully elucidated.

The nitrososulphuric acid bleaching process is one of historical interest. It was discovered by Guinon and Marnas about sixty years ago, and is frequently used in France. According to Silbermann, 1% of nitrososulphuric acid ("crystals of the leaden chamber") of 70° Bé. strength is dissolved in cold water and well stirred, the silk being entered at once and bleaching immediately. The silk is thereupon washed, and afterwards sulphured. The present author cannot recommend this process, since its success depends on the maintenance of a low temperature, and therefore artificial cooling may be required. Unless this precaution be observed, brown fumes of nitrogen tetroxide are easily disengaged in the bath, and not only nullify the bleaching action, but may also be injurious.

Hydrogen peroxide, which was long used for bleaching silk and is undoubtedly an excellent bleaching agent, is too expensive by comparison with others, and is therefore only employed in the case of silk with yellow bast (not for mulberry silks). It now, however, finds extensive application in the bleaching of spun silk and Tussah (*q. v.*).

Since hydrogen peroxide is decomposed by contact with metals, it must only be used in wooden or stone vats, or vessels of enamelled iron. The bleaching liquor is rendered slightly alkaline by an addition of ammonia or water glass. To obtain the full effect, the silk should be entered at hand temperature, and the bath gradually raised nearly to boiling point. If this does not produce the desired bleaching, the strength of the peroxide must be increased accordingly, or the operation be repeated, either in a fresh bath or in the correspondingly strengthened original one. The proportion of hydrogen peroxide in the bath is 1 : 30, and baths may be used over and over again after being made up to the proper strength.

Sodium peroxide is seldom used for bleaching mulberry silks, but is employed for Tussah and spun silk.

The electric bleach does not appear to have found any permanent application for silk bleaching.

LOADING

The loading of silk with the deliberate intention of deceiving the purchaser is a task which falls on the silk dyer. Since this practice will probably never be abandoned, it cannot be passed over without mention here, and it will be necessary for us to make the acquaintance of the materials which are used for loading, and learn the conditions these materials must comply with in order to meet the requirements they have to fulfil.

One of the peculiarities of silk is its capacity for absorbing large quantities of various substances and retaining them mechanically with a certain avidity, without exhibiting any alteration in its external appearance. The best known of these substances are sugar and tannin, both of organic nature and relatively low specific gravity. Loading silk with sugar is an old practice, but the resulting increase in weight is only small and of but little industrial advantage. Attention was therefore directed to inorganic substances of high specific gravity, which would leave the external appearance of the silk unaltered; and such substances were discovered in certain salts of tin and iron, which exceeded the highest expectations and enabled the silk to be loaded to as much as 1000 %. The increase in weight is accompanied by an increase in volume, the silk fibre swelling up so as to appear plumper, thicker and stronger. This is just what constitutes the objectionable feature of loading, the customer who purchases a "heavy" silk of this kind believing it to be a particularly strong, solid, firm and good article, whereas it is, in fact, weak and inferior. Not only does the absorption of the loading ingredients—often in multiples of its own weight—lower the mechanical strength of the silk fibre, but also alters it chemically. In all circumstances, loading silk with such active agents as tin chloride or the reducing ferrous salts has an unfavourable effect on the strength of the fibre. This is shown by the tendency of loaded silks to perish (rot), crumble to powder, and also to ignite spontaneously. Insurance companies, carriers, customs officials and warehouses have had very unpleasant experiences with loaded silks, and, with perfect justice, class them as highly inflammable goods, numerous fires having been caused by the spontaneous ignition of these silks. This fact alone is sufficient to pronounce sentence on the practice, which is condemned on the grounds of experience and common-sense, but without avail. There are some things against which even the gods strive in vain. There can be no change for the better until the purchasing public unanimously rejects loaded silks, and categorically insists on having only those that can be guaranteed free from loading ingredients. Regarded from any point of view, and taking into consideration all the factors which may make loading excusable on technical grounds, this morally and legally highly objectionable practice is a stigma on the silk industry.

At the present time the substances used for loading silk include sugar (as cane sugar, grape sugar or molasses), tannins (tannin, sumach or gallnuts for light shades, and sumach for dark), stannous and stannic chloride (for the most part wrongly termed "pink salt"), iron salts (ferrous pyrolignite and basic ferric sulphate), sodium phosphate and water glass.

Whether sugar, tannic acid, tin salts or salts of iron are used in practice depends in part on the quality of the particular silk in question, and in part on whether the loading is effected before, during or after dyeing; and, finally, on the degree of loading desired and the colour (light or dark) of the dye. Iron is suitable only for blacks or greys, and as loading with this metal is performed in the dyeing process, it will be described when dealing with the latter.

Loading with Sugar.—This, the oldest method of loading, is restricted to very light coloured silks, and rarely increases the weight by more than about 10 %. Cane sugar is used for pure white silks; grape sugar for cream and similar shades, and molasses for medium tones. The concentration of the sugar solution depends on the degree of loading desired, and varies between 10 and 12° Bé. The loading obtained is from 5 to 15 %, according to the strength of the solution and whether organzine, trame or chappe silk is being treated. Apart from the relatively small increase in weight produced, sugar loading has several disadvantages. The affinity of silk for sugar is not particularly great, and the sugar is not very securely fixed. To make an improvement in this latter effect, a little albumin is sometimes added to the bath; and sulphate of magnesia is commonly added, not for the purpose of loading, but to render the sugar-loaded silk less appetising to flies and bees. When sugar is used, the loading is always effected after dyeing. With the small increase in weight obtained the fibre does not swell; and, moreover, the method is rather expensive, so that it is now only occasionally employed. In order to ensure uniform distribution of the sugar, the silk must be well smoothed.

Loading with Tannin.—The capacity of silk for absorbing tannin is much greater than for sugar, a loading of 15–20 % being easily obtained. The operation is conducted either concurrently with or after dyeing, because if performed earlier the greater portion of the tannin would be extracted again in the dyeing process, and at the same time the capacity of the silk for absorbing the dyestuffs would be reduced. Tannin is used for white and cream silk, bleached sumach extract or gallnut extract for colours, and the unbleached extracts for dark shades. On the average, 2 parts of extract are taken for each part of silk, and the bath proportions are 1 : 30. The silk is entered at boiling heat, worked about well a few times, and then left in the bath till perfectly cold, being on no account removed earlier. The spent bath can be used over again after having been made up to the proper strength.

The aforesaid 15–20 % of loading applies only to cuite silk, souple being able to absorb much larger quantities of tannin—up to 50–80 %, and even 100 %. The loading may be effected in the softening bath, either during the softening or the dyeing process; or all three operations can be performed simultaneously, in the one bath. In some cases the silk is loaded in an extract bath (2–10° Bé.), and dyed and softened in an extract bath containing cream of tartar. The tannin baths for souple silk, however, must not be boiling hot, or part of the bast may be removed. The operation is carried on at 60–70° C. until the silk has become soft enough, whereupon it is left in the bath until quite cold.

Cutch is preferred for dark shades, 150 % of the weight of the silk being used, and the material left in the bath over-night, to be washed out in the cold next morning.

If a higher loading than 80 % is desired from tannins, prepared gelatine is used. Silbermann gives the following method of making the preparation: 6–7 parts of nitric acid (36° Bé.) are mixed by degrees with a thick solution of 50 parts of gelatine, and kept on the water bath for an hour at 60° C., taking care not to exceed this temperature or decomposition may set in. When cold, 5–6 parts of carbonate of soda are added, until the reaction of the mass is only faintly acid, and it is then diluted with 100 parts of water. For loading the silk a bath is prepared with 15–20 % of tannin (for light shades, and gallnut or sumach extract for dark), bast soap being added, and the solution soured with sulphuric acid after boiling. The dyestuff having been added, dyeing is begun at 50–60° C., and is continued until the desired shade has been attained. The bath is then boiled up again, the gelatine preparation (10–15 % of the weight of the silk) added and well stirred, and the souple silk entered and worked about quickly. In this way a loading of over 100 % is obtained. The bath can be used again, after being replenished with tannin. The chief advantage of this method is that tannin baths of low concentration can be used, thus preventing the dulling of the colours.

If still higher loadings are required, recourse must be had to metallic salts as well.

The above loadings with vegetable substances are unjustifiably termed "natural" loadings; those with metallic salts being called, with equal inaccuracy, "artificial." Combinations of vegetable and mineral loadings are known as "mixed."

Mixed Loading.—Since tannin loadings will not stand washing, and, for the most part, do not give much increase in weight, tannin loading is frequently combined with treatment with metallic salts, which also make the tannin fast to water. The metallic salts coming under consideration for this purpose are stannic chloride[1] for colours, and iron salts for black, gallnuts or sumach extract being used as the tannin in the former case, and cutch or chestnut extract in the latter. Mixed loading is effected previous to dyeing, and is preferably applied to cuite silk. It is also equally applicable to soft silk, care being taken not to have the baths too hot—to prevent loss of sericin. The best-known combination is tannin and stannic chloride, the silk being entered first in a chloride bath of 25–30° Bé. strength and then in a tannin bath. The resulting tin stannate is, however, yellowish, and this coloration is assumed by the silk. Moreover, silk loaded in this way will only absorb acid dyestuffs with difficulty; and since stannic chloride is well known to have an injurious effect on the silk fibre, this method of loading is only employed to a small extent. A more important combination is that of cutch and stannous chloride, which is very largely used. It forms part of the process of dyeing silk black, and will be described in detail in connection with that process, as well as the mixed loadings with cutch or chestnut extract and iron salts.

---

[1] In dyeing practice, stannic chloride is often called "pink salt," an erroneous description which is likely to produce confusion. The true "pink salt" is tin-ammoniochloride ($SnCl_2$-$2NH_4Cl$, or $SnNH_4Cl_6$), which can also be used for loading, but has been almost entirely superseded, for this purpose, by stannic chloride, $SnCl_4$. Pink salt contains 70·8% of stannic chloride, whereas the hydrated commercial chloride ($SnCl_45H_2O$) contains 74·35%. In respect of their tin content, these two products are therefore almost identical.

Tin Loading.—In all cases where white or pale dyeings are in question, combined with relatively heavy loading, tin salts must be used, the operation being performed before dyeing. The object of loading with tin is to accumulate tin oxide in the silk fibre. Hard silk (écru) is well wetted in warm water, pure silk (cuite) in cold, and then entered in a bath of stannic chloride [1] ($SnCl_4$, $5H_2O$) of 25–30° Bé. strength, where it is left for 1–2 hours after working about a few times at the outset. At the end of that time it is thoroughly washed in a circular washer and then treated for a half to three-quarters of an hour with a 25–30 % solution of carbonate of soda at between 40 and 60° C., followed by washing and re-entering in the tin chloride bath, which has, in the meantime, been made up again to 30° Bé. This cycle is repeated until the desired loading has been attained. Though simple, this method is objectionable because the deposited tin hydroxide [2] is very injurious to the silk. On exposure to direct sunlight, such silk will rot and crumble to powder in a few days—or even a few hours if heavily loaded—which is a plain warning against the use of this method. Tin loading is generally effected on the raw, unboiled silk, scoured silk having, strange to say, but very slight affinity for tin hydroxide, and absorbing only inappreciable quantities after the first bath. Souple and écru, on the other hand, will take up large amounts, the sericin, being a slightly acid substance, manifesting its affinity for metallic bases by readily absorbing them. The best way of completing the treatment is to enter the silk, after the final loading bath, in a bath of ammonia (instead of soda) at 80° C., wash, then in a soap bath containing ammonia, and finish the scouring in one or two soap baths.

---

[1] Stannic chloride is frequently termed "tin nitrate," because it is prepared by treating stannous chloride ($SnCl_2$) with nitric acid. The resulting product, however, contains no trace of nitric acid. Since the acid used acts solely as a reducing agent, it may be replaced by chlorate of potash, the final product in either case being $SnCl_4$.

[2] Opinion differs as to the decomposition of stannous chloride in washing, some holding that the hydroxide is deposited on the fibre, whilst others take the view that a basic stannic chloride or tin oxychloride ($Sn(OH)_2Cl_2$) is thrown down, and is then transformed into α-stannic acid ($SnO(OH)_2$) by the alkali.

Tin Phosphate Loading.—The serious injury done to the silk fibre by the accumulated free tin hydroxide, or the stannic acid—viz. the rotting of the fibre and the rapid loss of all its good properties—together with the considerable loss of stannic chloride in rinsing and scouring, led to attempts to discover a new method of tin loading. The idea suggested itself to combine the free hydroxide with a weak acid; and for this purpose, phosphoric acid has been found useful. Previously, a concurrent loading with tannic acid had been tried, in order to neutralise the injurious action of the tin; but, as we have already seen, the resulting tin stannate is yellow, and the method was therefore unsuitable for white and light shades. The tin phosphate which is formed by treating tin-loaded silk with disodium phosphate is, however, pure white. The operation is performed as follows: The half-scoured silk is treated in a bath of stannic chloride (25–30° Bé.), as in the ordinary practice of loading with tin; but instead of then using a soda bath, the silk is treated in a bath of sodium phosphate (3–5° Bé.). The bath temperature is maintained at about 75° C. for one-half to three-quarters of an hour, and raised to boiling for half an hour longer, the silk being finally rinsed. If required, the goods are returned to the replenished tin bath, and the cycle of operations is repeated 3–4 times, according to the amount of loading desired. By this means the silk can easily be loaded to 100–120 % above par. This treatment not only protects the fibre much better than in the old method, but also increases its characteristic lustre considerably, so that the method is a great improvement on the former one. The stannic chloride and sodium phosphate react, forming tin phosphate and sodium chloride. The reaction, however, seems to be accompanied by another, the tin bath becoming progressively more acid each time the silk is entered, the free hydrochloric acid formed accumulating to such an extent that it dissolves out the tin phosphate from the fibre, and thus renders the loading illusory. It is therefore essential to guard against this by neutralising the free acid with ammonia each time the silk is entered in the tin bath. Another difficulty which has to be overcome is in making up the tin bath to proper strength, the loss of density through the absorption of tin by the silk being compensated by the ammonium chloride derived from the ammonia added as neutralising agent, so that the liquor has an apparent density of 25–30° Bé., when the actual tin content corresponds only to one of about 5–10° Bé., the other 20° being due to the ammonia salt. Consequently, the specific gravity instrument is useless as an indicator of the strength of the bath, and a direct test must be made with a small hank of silk, by weighing it before and after passing through the bath, and estimating the tin strength from the difference. At the same time it affords an indication of the amount of sodium phosphate required to convert the tin hydroxide into phosphate. Theoretically, 716 parts of crystallised sodium phosphate are needed for transforming 182 parts of stannic hydroxide, whilst the same amount of phosphate will only transform 351 parts of stannic chloride. When the tin bath has become too concentrated for further use it is sold to chemical manufacturers, for the recovery of the tin. This might, perhaps, be done by the silk dyer himself, because it contains tin ammonio-chloride (pink salt) and sal ammoniac, which can be separated by fractional recrystallisation, the recovered pink salt being then available for preparing tin baths.

A remarkable circumstance, and one not yet fully elucidated, is that more tin is absorbed by the silk in the second and following tin baths than in the first one. Consequently, the amount of sodium phosphate added after the final tin bath is increased by 25–30%, the surplus being afterwards decomposed with sulphuric acid. After loading, the silk is thoroughly washed in the machine, and then dyed in the usual bast soap bath, soured with acetic acid. A bath of Marseilles soap and sodium phosphate is just as frequently employed.

Tin phosphate is not so injurious to the silk fibre as the stannic chloride and soda method, though it is quite harmful enough, especially under the influence of light. Many attempts have therefore been made to counteract or ameliorate these injurious effects of tin loading, and success appears to have been attained by two different methods. Weiss, the manager of the large silk-dyeing works at Thalwyl, on Lake Zürich, treats the loaded silk with a solution of ammonium sulphocyanide, whilst the manager of the Milan school of sericulture employs a solution of thiourea, both of which lessen the corrosion. Whether the destructive action of the loading is entirely prevented, the author has been unable to ascertain.

Phosphate-Silicate Loading.—The tin phosphate method was further improved by the modification introduced by H. J. Neuhaus Nachfolger, Crefeld (Ger. Pat. 75896). The stannic chloride bath is the same as for the phosphate method, but the sodium phosphate bath is soured and warmed, so as to precipitate acid tin phosphate on the fibre. It is claimed that this salt is capable, in turn, of taking up considerable quantities of silicic acid from its solutions. Whereas the loading effect of tin phosphate can be explained, chemically, in a simple manner, this is not the case with the silicate method. There is no chemical explanation why acid tin phosphate—even assuming that this is really present on the fibre—should absorb so much silicic acid as to give an increase of 100–120 % in weight on soft silk with five repetitions of the treatment. Moreover, the statement that a mixture of tin phosphate and tin silicate is present on the fibre, does not sound very plausible, for it is not very probable that the acid tin phosphate should react with sodium silicate in such a way as to take up any large amount of silicic acid from the latter. If that were so, it must cede aliquot quantities of phosphoric acid in exchange, which would not be very profitable. It would really be better to omit the expensive sodium phosphate entirely and enter the silk from the tin bath into one of water glass direct. The method is said to be applicable to all kinds of silk, in the hank and in the piece. The chief objection seems to be the large quantity of silica, since this may be assumed to make the silk hard. No record of the properties of tin silicate can be found in the literature; nor, from the quantitative point of view, does there appear to be any advantage over the tin phosphate method, which also gives a loading of 100–120 %, and does this in two baths, whilst the silicate method requires three.

Iron Loading.—This is only practised in conjunction with black dyeing, the two operations being inseparable. Combined iron and tannic acid loadings are in special favour, cutch and chestnut extract playing an important part. Combined tin and iron loadings are also practised, as well as complicated methods in which iron, cutch, tin and logwood take part. These, however, are empirical, each works having its own recipe which it considers superior to any other. Perhaps this is really so; if not—not. The black dyeing of silk will be dealt with later.

Other methods of loading have only a theoretical interest at present.

The high molecular weight of the salts of barium and lead may render them suitable for loading purposes, but their poisonous nature is against their application. Bismuth salts, being non-poisonous, would be admirably suitable, but are too expensive so far, and therefore the agents described above must be retained.

It has also been proposed to use zirconium salts and the thorium waste from incandescent mantle manufacture for loading silk. The basic salts of these two metals exhibit a tendency to deposit on the fibre, in the gelatinised state, thus effecting the loading in a very simple manner. Since there is no other means of utilising these salts and waste products, and they are consequently cheap, besides having no injurious effect on the silk fibre, experiments with a view to their employment would not be out of place.

Loading Cuite Silk.—This material is loaded, prior to dyeing, with tin, or tin and tannin, mostly by the phosphate method, or, for dark shades, with cutch and tin salt. In loading concurrently with dyeing, tannic acid alone is used; and after dyeing, loading is effected with sugar only.

Loading Souple Silk.—In this case, loading is rarely done before dyeing, the usual practice being to load and dye at the same time as the silk is softened. In general, souple is far more suitable for loading than cuite silk, as it takes up the loading agents, often in astonishing quantity, and gives results that are positively fraudulent. Happily, the tendency of late is to abandon excessive loading,[1] though loading up to 100–120 % above par is still considered perfectly fair. It must be evident, however, that souples and écrus loaded to this extent cannot last very long; and it is just these heavily-loaded souples that have given rise to the only too well-founded mistrust and prejudice against silk fabrics, formerly so durable and solid. No matter how many technical reasons may be urged in support of the loading of silk, the practice constitutes a serious wrong, and the more so because there is no necessity for it in any case.

Loading Hard and Raw Silk.—Raw silk and écru are loaded before scouring, the methods, in other respects, being the same as for softened silk.

PHYSICAL AND CHEMICAL PROPERTIES OF SILK

The raw silk coming from the reel is a white, yellow or orange-yellow, hard, stiff and dull filament of varying thickness. It is composed, as already stated, of the actual silk fibre, fibroin, and an envelope or sheath of so-called sericin, in the proportion of 75–70 % of the former, to 25–30 % of the latter. A fact less well known is that discovered by Bolley, viz. that the filament as spun by the silkworm consists entirely of fibroin. Logically, therefore, the sericin must be formed from the fibroin at a later stage, presumably by the action of atmospheric oxygen, accompanied or succeeded by hydration (absorption of water from the surrounding air). This conclusion is confirmed by analysis. Fibroin corresponds to the formula $C_{15}H_{23}N_5O_6$, sericin to the formula $C_{15}H_{25}N_5O_8$, the change being expressed by the equation :—

---

[1] Under an agreement between the Crefeld and the Swiss silk manufacturers, organzine is not to be loaded to more than 24–30 % above par, whilst Japanese and unsoaped China weft are not to exceed 60–80 % above par. Where the weft is to be used for taffeta weaving, these maxima are reduced to 50–60 % for Japanese and white, unsoaped China weft.

$$\underset{\text{Fibroin}}{C_{15}H_{23}N_5O_6} + O + H_2O = \underset{\text{Sericin}}{C_{15}H_{25}N_5O_8}$$

It will be apparent that this transformation is most complete on the surface, and that it will not be so great in the immediate vicinity of the internal fibre; that is to say, intermediate layers will occur between the fibroin and the sericin. This is confirmed by the fact that, in scouring the raw silk, the first bath never removes the whole of the sericin, but only about 18–20 % at the most, whilst the remainder is not dissolved before the second bath, having apparently been transformed meanwhile into the more readily soluble form of sericin. Although its solutions do not exhibit an acid reaction, sericin clearly behaves in other respects like a weak acid, being readily and completely soluble in even weak alkalis, whereas it is nearly or quite insoluble in acid liquids, though swelling up therein. The scouring of silk is based on the former property, and the second is utilised in the softening process.

Fibroin, on the other hand, is completely insoluble in pure water, but dissolves in strong alkalis and mineral acids, zinc chloride, ammoniacal nickel protoxide or ammoniacal copper oxide. This behaviour of silk towards certain solvents is utilised in chemical tests for detecting and separating silk in presence of other textile fibres. Raw silk contains 66–75 % of fibroin, which substance is of proteid character and is also found in other fibres spun by insects.

The fibroin completely freed from sericin constitutes the true silk fibre, cuite or pure silk, the noblest and handsomest of all textile fibres. Its most valuable property is the characteristic lustre, due to the incomparable manner with which it reflects the light. This, of course, is true of pure silk only, the filaments exhibiting a correspondingly diminished lustre in proportion as they are still surrounded by sericin. This silky lustre can be impaired, and even entirely destroyed, by a number of causes, loading with tannin having the former effect, and loading with stannic chloride and soda removing it altogether. Remarkably enough, tin phosphate loading, on the other hand, increases the lustre of silk, a peculiarity which has not yet been explained.

The colour of the pure silk fibre is white. The apple-green, yellow and orange colour of many raw silks is due to the natural pigments in the sericin, the fibroin being white in these cases as well. It may happen, however, that, through the fault of the dyer, this natural colouring matter finds its way into the silk fibre, especially when the scouring is conducted at too high a temperature, and in this event the colouring matter is fixed by the silk. Apart from lustre and colour, the feel of silk is distinctive, and, like the lustre, is peculiar to pure silk. It cannot be described in words, but implies the sensation produced when the silk is touched or handled. It depends chiefly on the way the silk is treated in scouring, bleaching, loading, and dyeing. The so-called "scroop" of silk is not a characteristic property and is only observed in scoured silk that has been treated with weak acids (acetic, tartaric, citric or boric) prior to washing out the soap used in scouring. " Scroop " is therefore due solely to the above treatment, and is never found in silks that have been treated in alkaline baths.

Morphologically, silk is a simple, smooth, structureless, homogeneous, solid fibre ; a smooth, somewhat flattened cylindrical double filament, similar to that of artificial silk, but with the difference that the latter is single. Silk fibre is highly elastic and can be stretched out by $\frac{1}{7}$ to $\frac{1}{5}$ beyond its normal length without breaking. The elasticity of scoured silk is 45 % below that of raw silk. Since the lustre is improved by stretching, this operation is one of the most frequent of the mechanical treatments to which silk is subjected in the course of manufacture. The property of softness is exhibited in the highest degree by fully-scoured silk, and varies in inverse proportion to the amount of sericin allowed to remain, being also impaired by stretching. The fineness of silk depends on the number of cocoon filaments twisted together in reeling. For spinning purposes the fineness is expressed by the " titre " or weight of a given length of fibre.

The tensile strength is higher than that of any other textile fibre, the breaking length of raw silk being 30·8 kilometres ; that is to say, in order to break under the strain of its own weight when hanging freely, without any artificial loading, a silk thread would have to be nearly 19 miles long. A thread with a sectional area of 1 sq. millimetre will break under a load of 35–44 kilogs. The elasticity and tensile strength of silk are measured by means of the serimeter. In correspondence with its tensile strength, silk has a high power of resisting climatic influences ; it putrefies with great difficulty and is rarely attacked by moths, but, on the other hand, it is rather susceptible to mildew.

Silk is a bad conductor of electricity, and is therefore used for winding round electric wires in order to reduce the loss of electrical energy. In perfectly dry air, pure silk is absolutely non-conducting, but this is not the case when it has been dyed, especially black. The specific gravity is relatively low, being the smallest of any of the textile fibres, and scoured silk is specifically lighter than raw silk. Statements as to the specific gravity vary considerably, the values ranging, according to Vignon, from 1·163 (Canton raw silk) to 0·885 (scoured Canton silk). The value changes, of course, during the chemical (bleaching, loading, dyeing, brightening) and mechanical treatments (stretching, lustring, smoothing, etc.) to which the silk is subjected.

Silk is porous, and can therefore absorb not only atmospheric moisture in fairly large amount, but also other gases, such as water vapour (to a greater extent than water in the liquid form). Gases of decidedly basic or acid character are absorbed in not inconsiderable quantities: for example, ammonia, hydrochloric acid, sulphur dioxide. It also absorbs liquids, especially water (up to 30 %), and retains them tenaciously. The maximum permissible amount of moisture in silk is 10–11 %, anything in excess of this figure reducing the value. For this reason, the determination of the water content is an important factor in fixing the value of silk. The test is known as "conditioning," and is performed in special conditioning houses.

The absorptive capacity of silk for liquids and saline solutions also constitutes the basis for the operation of mordanting with salts of iron, aluminium and chromium, as well as loading with stannic chloride and tannin solutions. Tannins seem to produce a tanning effect on the fibre, manifested by a diminished capacity for absorbing dyestuffs.

The chemical composition of silk is given by the following ultimate analysis :—

	Staedeler.	Gerhardt.	Cramer.	Schützenberger.
Carbon . .	48·60	48·53	48·39	48·60
Hydrogen . .	6·40	6·50	6·51	6·30
Nitrogen . .	18·89	17·35	18·40	18·70
Oxygen . .	26·11	27·62	26·70	26·25

On ignition, pure silk leaves a small quantity of ash, raw silk furnishing 0·75–0·78 %, consisting of phosphates, sulphates, chlorides, carbonates and silicates of aluminium, iron, calcium, magnesium, potassium and sodium.

Water has no action on silk, which is completely insoluble therein even after prolonged boiling, though it weakens the fibre. On the other hand, silk that has been damped with water and exposed for a long time to the air, becomes slightly soluble, through the absorption of water and atmospheric oxygen into the fibroin, sericin being formed.

Alcohol is greedily absorbed and tenaciously retained by silk, but has no solvent action. Acids, especially in the concentrated state and when warm, dissolve silk or destroy it. Boiling hydrochloric acid of ordinary strength dissolves silk quickly and completely (distinguishing test in comparison with wool); gaseous hydrochloric acid destroys the fibre, but very dilute HCl has little or no action. Strong nitric acid destroys it completely at once, but dilute nitric acid containing nitrous acid merely stains the silk a yellow colour which is fairly fast to light and completely so to water. On the other hand, chemically pure nitric acid does not produce any such coloration. Nitrous acid probably converts silk into diazofibroin. Concentrated sulphuric acid dissolves silk to a brown syrup which forms a clear solution with water; but dilute acid has practically no action. Sulphurous acid, preferably as vapour but also in aqueous solution, bleaches the silk fibre. A cold-saturated solution of chromic acid, diluted with its own volume of water, oxidises and completely dissolves silk after boiling for 1 minute (von Höhnel). At high temperatures, silk is readily and completely dissolved by glacial acetic acid, fused oxalic acid and citric acid. Caustic alkalis, too, quickly dissolve silk completely in the warm, though concentrated solutions have practically no action at 0° C. Dilute acids merely cause the silk to swell up, a small portion passing into solution. Ammonia has no appreciable action, even on heating. Prolonged treatment with a solution of caustic lime makes silk brittle, and finally destroys the fibre. Alkali carbonates act less powerfully than caustic alkalis, and ammonium carbonate is inert. Neutral soap solution dissolves only the sericin when warmed, though prolonged boiling also corrodes the fibroin to some extent. Very weak alkalis, like borax and water glass, dissolve the sericin without attacking the fibroin. Chlorine and soluble hypochlorites destroy silk easily and quickly, and consequently must not be used for bleaching that fibre. The alternating action of hypochlorite solution and air containing carbon dioxide does not destroy the fibre, and improves its capacity for taking up dyestuffs. The chemical action seems to be similar to that in chloring wool. Certain metallic salts are partially decomposed by silk, which behaves like wool in this respect. Solutions of aluminium, chromium, and iron salts are deposited in the fibre as basic, sparingly soluble compounds, even at ordinary temperature (distinction from wool). Silk also seems to resemble wool in playing the part of a weak acid. The mordanting of silk (*q. v.*) is based on the aforesaid property of partially decomposing metallic salts. Solutions of certain salts dissolve silk completely without alteration, chief among them (according to Persoz) being a 60° Bé. solution of basic zinc chloride, which transforms silk fibre into a thickish, gelatinous fluid, slowly in the cold but quickly and easily in the warm. On diluting this solution with water, the fibroin separates out as white flakes, which, when the zinc chloride has been washed out, are soluble in ammonia. If the washed flakes are dried at 110–115° C., they become hard and glassy and are no longer soluble in ammonia. Zinc chloride solution of the above strength does not dissolve either wool or cotton, and this test has therefore been recommended by Remont for the separation and determination of silk in presence of other textile fibres. For this purpose it is desirable to use a solution of 100 parts of zinc chloride in 85 parts of distilled water, 4 parts of zinc oxide being dissolved in the clarified solution. A 45° Bé. solution (sp. gr. 1·45) of zinc chloride dissolves pure silk rapidly, but Tussah silk only after a time, and this solution can therefore be used for separating the two. Still weaker solutions have no solvent action, but produce crépon effects. A solution of ammoniacal copper oxide behaves in the same manner as zinc chloride. According to Péligot, an excellent solution of this kind is obtained by dissolving copper filings—or, better still, finely-divided electrolytic copper powder—in strong ammonia, taking care that air is freely admitted. This solution dissolves both silk and cotton in the cold, but wool only on heating. From the cold solution, cotton is reprecipitated, as cellulose, by neutral salts, sugar or gum, but silk is not thrown down by any of these agents. According to Schlossberger, an ammoniacal solution of nickelous oxide readily dissolves silk, but leaves cotton intact. Hummel recommends an alkaline solution of copper and glycerine as an excellent solvent for silk, whereas cotton and wool are left undissolved. The solution is prepared by dissolving 16 grms. of copper sulphate in 140–160 c.c. of distilled water and 8–10 grms. of pure glycerine, caustic soda solution being added, drop by drop, until the precipitate first formed is just redissolved. The caustic alkali must be added carefully, to avoid excess. In the dry state, silk is not so susceptible to the action of heat as wool, and though it parts with the final traces of moisture at 110° C., it remains otherwise unchanged. At temperatures above 170° C. it decomposes rapidly with partial carbonisation. Permanganate of potash has an oxidising effect, manganese perhydroxide being, at the same time, deposited on the silk fibre.

Estimating the Value of Silk

To ascertain the commercial value of silk, the chief factors, next to the external appearance, are the moisture content and the degree of fineness, these last two values being found by conditioning and by determining the "titre."

The operation of conditioning is carried out in special conditioning houses. A certain quantity of the silk is weighed out and placed in the conditioning apparatus, where it is freed from moisture by dry air (heated to 100° C.) until of constant weight, the difference between the initial and final weighings giving the absolute percentage of moisture. The standard, instead of being absolutely dry silk, is silk with 11 % of moisture; that is to say, silk containing 89 % of dry substance, the commercial weight of the silk being found by adding 11 % to the ascertained weight of perfectly dry silk. *Example:* A silk loses 18 % of its weight in the conditioning process, and therefore 100 parts by weight contain only 82 of perfectly dry substance. The commercial weight, however, would be 91 (82·0 + 8·2 + 0·8), and 100 parts of such silk would only be equivalent to 91 parts of a silk of standard moisture content.

The "titre" expressing the fineness of both raw and thrown silk is determined by ascertaining how many times a given length (475 metres) of the thread go to make a certain unit weight. The "count" of silk threads represents the absolute weight of 475 metres of the fibre.

MECHANICAL OPERATIONS IN SILK DYEING

Before going into the chemical aspect of silk dyeing, a brief account will be given of the mechanical treatment of the fibre in that process. Silk is chiefly dyed in the hank, although latterly the practice of dyeing in the piece has made headway. The first step is to bind a number of hanks together with a strong cotton thread. In the dye-bath the hanks are worked about by hand, for which purpose they are placed on smooth wooden pins. Owing to the delicate nature of the fibre, all roughness on the pins must be avoided. Artificial polish soon wears off through contact with the hot liquor, and naturally smooth wood, such as cane, bamboo, etc., is therefore preferable. When the hanks are turned, that portion which was previously at the bottom of the loop must be placed against the pin, and at the same time the hank must be pulled out straight and stretched in order to prevent tangles. Pins are only used in the case of corrosive baths, such as stannic chloride, if the operator does not desire to wear rubber gloves. Two to five hanks are suspended from each pin, according to the width of the dye-vat. In addition to being worked about, the hanks are lifted from time to time and re-entered in a different part of the bath, the work being usually performed by two operatives. The fineness of the threads making the hanks very liable to get tangled in the bath the dyer must smooth and open them at intervals, carefully separating them by hand on the wringing post and then beating them with the pin. This operation is, to some extent, a modification of the stretching process. Rinsing is carried out by hand in the usual way, but washing is generally done in the machine. Then follows draining or squeezing, to remove the bulk of the washing water, and after that, centrifuging in the hydro-extractor.

Before proceeding to dry the hanks they are stretched, to restore the contracted fibres to their original length and arrange them in parallel position. Stretching is always done by hand, with the aid of the wringing post in the same way as "opening."

Lustring, the next step, is a modified form of stretching, but is performed in a machine. Besides slightly stretching the fibre, it greatly improves the lustre of the silk. The friction of the hanks against the polished metal rollers of the machine makes the fibres broader and flatter, an undesired effect which is counteracted by a short steaming, at ordinary pressure, in steaming boxes, whereby the normal roundness of the fibre is restored.

The hanks are then dried, and as silk is extremely susceptible to dry heat, and heat has an unfavourable influence on the surface tension, on which the lustre of the silk depends, high temperatures in the drying process must, as far as possible, be prevented. The best method is to dry the silk with dry, unheated air; and if drying chambers or stoves are used, the temperature should not be allowed to rise above 35° C. Moving the hanks about on the drying rods facilitates the operation.

Drying is succeeded by smoothing, preferably in a machine. This operation also may be regarded as a kind of stretching, but that action is accompanied by treatment which may be described as dry wringing, the hanks being simultaneously given a strong twist and stretched. This treatment causes the threads to rub together, and thus makes them supple. The operation is particularly employed in the case of softened silk.

In piece dyeing, the preliminary treatment includes gassing, to remove fine projecting fibrils and make the surface perfectly smooth; boiling or scouring in the same way as for hanks; rinsing in soda solution, then hot water, and finally in slightly soured cold water; drying; a second gassing, and then dyeing. In accordance with the valuable and delicate nature of silk, the piece goods are treated in the wide open condition, and of course with the care and precaution that such expensive material requires.

Dyeing Machinery and Appliances

Cleanliness, which is desirable in every dyeworks, is essential when silk is the material under treatment The high price of silk, coupled with its delicate nature, makes it necessary to exclude all rough surfaces in the appliances used. Thus, no wooden vats are used in silk dyeworks—at least well-equipped and modern plants—but only copper vessels, or wooden vats lined with copper. Sometimes a lining of jute cloth is used; but this is never as good as copper. Some old dyeworks are still to be found where wooden vats are used, or even copper pans heated by direct fire, and where the rooms are dark. A modern silk dyeworks should be roomy, well lighted, clean, and provided with steam-heating appliances. Since the silk has to be repeatedly stretched, opened and lustred, there must be no lack of wringing posts; and there must also be an ample supply of smooth dyeing pins, especially since hank dyeing is almost always done by hand. Hank-dyeing machines are rarely to be met with in silk dyeworks, though they are sometimes used for loading or soaping, particularly for operations in which the silk has to be moved about in the bath for a long time. The only hank-dyeing machine, out of the many designed for this purpose, that has come into any general use is that of Corron. Space will not permit a detailed description of these machines, which are fully dealt with in the author's work on the theory and practice of modern dyeing.[1]

Washing machines are more extensively employed, both in the form of hank washers and circular washers, the arrangement of which may be assumed to be known. The same applies to the centrifugal drier or hydro-extractor, and squeezing machines for forcing bath liquors out of the hanks.

Beating, stretching and smoothing are all carried out in special machines.

Piece dyeing naturally requires quite a different set of appliances, such as gassing machines, and scouring machines fitted with heating coils. The scoured piece goods are washed in the jigger, the best method being to arrange several jiggers in series, the first two being charged with soda solution, the next two with hot water, and the last two of the series with acidified cold water.

Draining is effected in a horizontal or wide-open hydro-extractor and dyeing in a wide-open machine. Special machines have been constructed for dyeing silk plush and velvet wide open. The pieces are dried in the cylinder machine.

The dyed pieces are usually finished by the dyer, in a number of different machines, according to the requirements sanctioned by time or imposed by current fashion. Since, however, finishing does not fall within the scope of the present work, there is no need to go into further particulars of these machines.

---

[1] A. Ganswindt, *Theorie und Praxis der Modernen Färberei*, Part I.: "Mechanische Technologie."

WATER IN SILK DYEING

Water is one of the most important and indispensable materials in dyeing—except in the so-called "dry" dyeing process. The dyer could not perform any of his tasks without water. He needs it in preparing the various baths; for washing, rinsing, feeding the boiler, dissolving dyestuffs and mordants, etc. Dyeing itself is carried on in baths prepared with water, this liquid being, therefore, the medium in which the actual reactions of dyeing proceed. Nevertheless, the majority of dyers fail to attach to water the importance which it has the right to claim. To say that "water is water" is a fallacy. One need only compare the water of two different towns (for example, Aachen and Zurich), where goods dyed under otherwise identical conditions give astonishingly divergent results, entirely due to the different character of the water employed. Take the case of boiler fur, which, after a boiler has been a long time in use, forms a crust as hard as stone, and demonstrates that the water must have contained substances—and that, too, in large quantity—which have escaped observation and which the colour, smell and taste of the water have failed to reveal. Water is recognised as a solvent of the first rank, capable of dissolving, and retaining in that condition, varying quantities of a large number of substances. Now, as water, before appearing on the surface of the ground, has to traverse a variety of strata, it has the opportunity of becoming charged with substances, both organic and inorganic; and this explains the variation in the composition of water in nearly all parts of the globe, the differences often being very considerable. Rain water comes nearest the ideal of chemically pure water, since it contains no solid constituents, and can be used direct for dyeing. Although the best water for this purpose, it is frequently unavailable in sufficient quantity, and, above all, in equal amount at all times. The dyer must therefore resort to river water, lake water, well water or town water, that is to say, waters which, almost without exception, contain solids in solution. Of these solids, the most objectionable from the dyer's standpoint are the salts of lime, magnesia, iron and manganese, these making the water unsuitable for most operations—though not all—in dyeing. The salts of lime and magnesia in particular are the cause of boiler fur, and impart to water the property known as "hardness." Hard water is highly momentous for the dyer when he is using soap baths, the lime and magnesia salts decomposing the soaps and forming insoluble alkaline-earth soaps, thus wasting the chief constituent of the bath. Now, the silk dyer works almost exclusively with soap baths, and hard water would ruin him. A supply of soft water is therefore indispensable in silk dyeing; and if this is not available on the spot, the local hard water must be softened for all operations in which soap, or even bast soap, is used. In other cases, hard water is applicable. As an example of the loss which hard water causes the silk dyer, it may be mentioned that 1 part by weight of lime present in water will decompose 13½ parts of ordinary soap, and that, in the case of river waters with an average of 10° of hardness, every 12,000 galls. used means a waste of 1 cwt. of best soap, or a correspondingly larger amount of commoner kinds. In the course of a year this will work out to a fairly respectable sum. In fact, it is estimated that some 275,000 tons of soap are wasted yearly, through the use of hard water, in Lyons alone. The silk dyer is therefore recommended always to soften his water if hard.

To ascertain whether a sample of water is hard, it should be mixed with an alcoholic solution of soap, in a test glass, and shaken up. Soft water will give the characteristic lather of soap, whereas hard water does not. To detect the presence of lime, a sample of the water is treated with a little ammonium oxalate, a white precipitate, or even turbidity, indicating lime. The quantitative determination of the salts of lime and magnesia causing the hardness entails a titrimetric test with alcoholic soap solution, which need not be further detailed, since the dyer will usually transfer this task to a chemist.

The purification of water consists chiefly in treating it with chemicals adapted to throw down the lime and magnesia salts as insoluble precipitates. These additions usually consist of lime-water and carbonate of soda (caustic soda being also used sometimes), the quantities used being calculated from the results of a preliminary analysis of the water. The treatment is applied in special appliances of various forms, which need not be described in detail.

Within the last few years, a new method of softening water has been introduced, namely, the permutite filter, which is based on quite different considerations and is therefore quite distinct from the older methods. The process may be described as a " contact process," inasmuch as the purification, or softening, of the water is effected by merely allowing the water to flow gradually through a " contact substance," just as in large municipal waterworks the water is allowed to percolate through alternating beds of gravel, sand and coal. The novelty and special feature of this new process consist in the contact substance employed.

The process is based on the observation made, more than sixty years ago, by the English agricultural chemist, Way, that heavy clay soil is able to decompose certain saline solutions by depriving them of their bases. This peculiar behaviour of the clay has been attributed to the presence of " zeoliths," a term applied by mineralogists to a group of natural hydrated silicates or double silicates of alumina. These substances, which are highly translucent and colourless, though occasionally white or coloured red or grey by the presence of impurities, and are of low hardness and density, have the property, when treated with acids, of parting with silica (mostly in the gelatinous form), and of fusing before the blowpipe, with considerable intumescence, to a distended white or colourless enamel. The double silicates contain soda or potash, in addition to alumina, and are presumably secondary natural products originating from feldspar and feldspathic rocks. They occur as handsome crystals, for example, in the Bohemian Mittelgebirge, in the Fassatal (Tyrol), and in Scotland. These double silicates are the sole active substances in the softening process under consideration.

Way's interesting observation was not pursued further at the time, and it is only quite recently that his statements have been investigated by prominent chemists. These investigations have revealed that the various zeoliths are by no means uniform as regards their powers of dissociation. Gans, in particular, has shown that Chabasite, a sodium zeolith, is the most active in this respect, and that it is, for example, capable of completely removing the lime and magnesia salts from hard water. He also demonstrated that the reaction is not one of dissociation, but double displacement, an exchange between the sodium atoms of the Chabasite and the calcium, or magnesium, atoms of the hard water. That is to say, the sodium zeolith is gradually transformed into a calcium or magnesium zeolith. This discovery proved beyond a doubt the suitability of Chabasite for softening hard water. At first, this proof did not attain any technical importance, Chabasite being rarely found in nature, and then not in workable deposits. Gans, however, proceeded to make, in the place of native Chabasite, an artificial alumina-soda silicate, by fusing together suitable proportions of soda, quartz and kaolin. The resulting melt is leached with hot water, for the purpose of hydration and to eliminate the soluble sodium silicate formed. The preparation is centrifuged, but not dried, being used in the form of paste. It forms a white, laminar-crystalline mass highly endowed with the property of completely extracting the lime and magnesia salts present in hard waters. Since the softening action of this artificial sodium zeolith depends on an exchange between its sodium atoms and equivalent quantities of the calcium or magnesium atoms of the hard water, the action must naturally become progressively weaker, in proportion as the zeolith becomes poorer in sodium. Consequently, it is not advisable in practice to continue using the zeolith until completely exhausted. The gradual decline in activity is manifested by the recurrence of estimable quantities of lime or magnesia salts in the treated water, lime being detected by adding a little ammonium oxalate. To test for magnesia, the water is treated with ammonium chloride and ammonia, followed by sodium monophosphate, with which magnesia gives a milky turbidity.

An important consideration now arises, namely, that when the active properties of the sodium zeolith have been exhausted, the material can be regenerated by a simple treatment with a concentrated solution of common salt. This causes a reversal of the previous reaction, the exhausted material, which now represents a calcium or magnesium zeolith, exchanging its base atoms with the sodium atoms in the salt, thus reconstituting the sodium zeolith, whilst the sodium chloride is transformed into calcium or magnesium chloride. The regenerated product can be used again and again for softening water, by repeating the regenerative treatment. However, certain other decomposition products are formed which deprive the sodium zeolith of the unlimited working life it would appear, theoretically, to possess.

This is one shady side of the process; another is that it is not directly suitable for the removal of temporary hardness, the carbonic acid of calcium bicarbonate tending to decompose the aluminium-sodium silicate and render it inactive. Consequently, the temporary hardness must be first removed, which is claimed to be effected by "filtering the water through marble;" which, however, is hardly imaginable. A more feasible and suitable method would be to transform the calcium bicarbonate into sulphate by treatment with sulphuric acid, followed by warming. The zeolith process, therefore, has its limitations, but nevertheless its simplicity makes it of interest, and it has already found its way into practice, the artificial sodium zeolith according to the Gans recipe being on the market as "permutite."

For removing iron from water, a manganese permutite filter has been introduced, consisting of pure calcium zeolith permeated with higher oxides of manganese. It is claimed that iron and manganese are completely removed from water passed through this filter, presumably by the oxidising action of the contained manganese oxides. When exhausted by prolonged use, the filter can be regenerated by treatment with potassium permanganate, which restores the reduced manganese oxides in the filter material to their higher stage of oxidation.

Recently, in addition to the permutite process, two others of the same category have come into notice: the "allagite" process and the "berrite" process.

CHEMICALS USED IN SILK DYEING

Considerations of space prevent more than a concise account of the chemicals used in silk dyeing, chief among them being: tin chloride, the iron mordants, alumina mordants, chrome mordants and tannin agents.

ACIDS

Sulphuric Acid.—The crude sulphuric acid of commerce is a clear, colourless to brownish, very acid, non-fuming liquid of oleaginous consistency and a sp. gr. of 1·83–1·84, which corresponds to a density of 66° Bé. It is miscible in all proportions with water, a considerable amount of heat being disengaged in the process. The acid must always be poured into the water, the latter being kept in motion—never the water into the acid. Sulphuric acid is strongly corrosive, and destroys animal and vegetable substances. If any of the acid gets on to the skin, it must be removed at once by the aid of plenty of water. In silk dyeing, this acid is used for souring bast soap baths and for livening colours.

Sulphurous Acid.—This acid is largely used, in the gaseous form (sulphur dioxide), for bleaching silk, and is produced, for this purpose, by the silk dyer himself, by burning rod sulphur in sulphur boxes. The sulphur burns with a faint bluish flame, forming sulphur dioxide which is colourless, has a penetrating and suffocating odour, and is poisonous when inhaled, on which account the sulphuring chamber must be thoroughly ventilated before being entered. A solution of this gas in water forms aqueous sulphurous acid, which is limpid, and has the same smell as the gas, of which it contains 3½–10 %.

Hydrochloric Acid.—A clear, yellowish liquid, which fumes strongly in the air, has a suffocating odour, very acid taste, and a density of 20° Bé. In silk dyeing it is used for making stannic chloride, the preparation of aqua regia, the production of nitrous acid in diazotising, and for brightening tannin-iron blacks.

Nitric Acid.—This acid is a clear, colourless to yellow liquid, which gives off strong fumes in the air and has a peculiar, disagreeable smell. It stains the skin, and silk, yellow. The commercial acid has the density 35–36° Bé. It is used for making stannic chloride and aqua regia.

Aqua Regia.—A mixture of 1 part of nitric acid with 3 of hydrochloric acid, which is yellow in colour and dissolves practically all metals except lead and silver. It is used for making stannic chloride and bleaching soft silk.

Acetic Acid.—In dyeing, use is made of the technical acid obtained by distilling crude calcium pyrolignate with sulphuric acid. It is a colourless, completely volatile liquid, with an acid and faintly empyreumatic odour. It is employed in the preparation of iron pyrolignite (black mordant) largely used in silk dyeing; for souring bast-soap dye baths; suspending basic dyestuffs; as an adjunct to the dye bath, and for livening colours.

Formic Acid.—A colourless, slightly fuming, strongly corrosive liquid, with a penetrating acid odour, solidifying at zero C., melting again at 8° C., and boiling at 99°. It is a more powerful acid than acetic acid, and can be used to replace sulphuric acid in souring bast soap.

Oxalic Acid.—This highly poisonous acid occurs as colourless and inodorous, small rhombic columns or needles, which are stable in air and are soluble in 9 parts of cold water and very readily in hot. It is sometimes used as an adjunct to alumina or chrome baths in mordanting silk.

Tartaric Acid.—Large, hard, white, translucent crystals, with a strong, but agreeable, acid taste, free from smell, stable in the air, and very readily soluble in water. It is used for livening dyeings with basic and eosine dyes.

Citric Acid.—This acid is used in the same way as tartaric acid.

Tannic Acid, Tannin.—Is absorbed in considerable quantities by both the silk fibre and the sericin, and therefore serves as a loading material. For white and light-coloured silks, the tannic acid obtained from gallnuts is the only suitable kind. Tannin is a yellowish or nearly white, loose, light, fine powder, with a faint, peculiar smell and slightly astringent, not acid, flavour. It is readily soluble in 6 parts of cold, and in its own weight of hot water, to form a reddish-brown solution. A form of tannin recently introduced, under the name of crystal tannin, is in beautiful lustrous, golden-yellow needles. For medium and dark shades the more expensive form of tannin is replaced by the raw materials from which it is prepared, *e. g.* gallnuts, sumach, divi-divi, etc. Tannin forms blue compounds with iron, but for black dyeings, preference is given to a tannic acid—such as is contained in cutch—which gives green colorations with iron. For leading silks, the tannic acids are either used alone or fixed on the fibre with the assistance of metallic salts, such as those of iron or tin. Strangely enough, salts of zinc or antimony, which furnish *white* tannates, have not yet found application.

BASES

Ammonia.—A colourless aqueous liquid, with characteristic pungent smell and strongly basic properties. Commercial ammonia contains 20 % of gaseous ammonia, has the sp. gr. 0·925, and is largely used in silk dyeing, for washing and cleaning the fibre, extracting or washing out fats and soaps, neutralising acid baths (for example, stannic chloride baths that have become acid), and for fixing alumina and chrome mordants.

Caustic Soda.—A yellowish, oily liquid, miscible in all proportions with water. It dissolves animal skin and makes it slippery. Owing to its strongly corrosive action on silk, its use is restricted to the necessary addition of lye in vatting vat dyestuffs with hydrosulphite.

Sodium Peroxide.—A yellowish-white to white powder, which hisses and gives off heat when dissolved in water. When boiled in water, it liberates oxygen, and hydrogen peroxide is formed on treatment with dilute acids in the cold. It is on this property that its application for bleaching silk and Tussah is based.

Lime.—This substance, both as quick and slaked lime, is sufficiently well known. In dyeing, it plays only a subordinate rôle, in the preparation of zinc-lime vats.

SALTS

Ammonium Salts.—Ammonium acetate, obtained by neutralising acetic acid with ammonia, is a colourless liquid, with a cooling, salty taste. In silk dyeing, it is sometimes used as a substitute for the bast-soap bath.

Ammonium Sulphocyanide (thiocyanate) occurs as colourless, readily deliquescent crystalline scales, and is used in the after-treatment of tin-loaded silks, in order to counteract, or at least ameliorate, the injurious effect of the loading agent on the silk fibre under the influence of sunlight.

Potassium Salts.—Potassium Chlorate takes the form of colourless crystalline flakes, sparingly soluble in cold water, but readily so in hot, readily ignited, and explosive. It is used as an adjunct in dyeing silk with aniline black.

Potassium Permanganate forms crystals which are black, with metallic lustre, in reflected light, and violet-red by transmitted light, dissolving easily to a purple-violet solution in water. It acts as a powerful oxidising agent, and is recommended as such for bleaching Tussah silk. Potassium chromate crystallises in large orange-yellow, anhydrous triclinal columns or plates, dissolving to a yellow solution in 10 parts of water. It is a powerful oxidising agent, poisonous, and serves for oxidising certain dyestuffs, and developing such colours as logwood black, cutch brown; also for the after-treatment of a number of acid azo dyestuffs on the fibre, completely oxidising emeraldine to aniline black, etc. Cream of Tartar (Potassium tartrate), in the purified state forms translucent, hard rhombic crystals or a white crystalline powder, of faintly acid taste and sparingly soluble in water. Is used in the preparation of soft silk. Potassium Ferrocyanide (yellow prussiate) forms large, soft, lemon-yellow quadratic prisms, soluble in 4 parts of water and possessing a bitter, but not ferruginous, taste. With ferric salts it gives an immediate deep-blue precipitate. It is non-poisonous. Plays an important part in "bluing" (black dyeing) silk, and is also used in the preparation of aniline black.

Sodium Salts.—Sodium carbonate is met with in commerce both as soda crystals and calcined soda, the latter being preferred in dyeing on account of its freedom from water of crystallisation and caustic soda. In point of activity, 10 parts of calcined soda are equal to 27 of crystals. Soda is strongly alkaline in taste and reaction, and the crystals are soluble in 1½ parts of water. For use in silk dyeing, it is essential that sodium carbonate should be free from iron. It is used in large quantities for fixing stannic chloride in loading silk with tin, and for softening water. Glauber salt (sodium sulphate) is sufficiently well-known to every dyer. Sodium Hydrosulphite is obtained as a greyish-white powder or a concentrated solution of the density 17° Bé. To prepare a solution of 17° Bé. strength, 10,000 parts of sodium bisulphite solution (38–40° Bé.), cooled with cold water or ice, are treated with 1300 parts of zinc dust, added by degrees, the mixture being stirred for half an hour at a temperature not exceeding 40° C. (104° F.). Milk of lime (prepared by slaking 1000 parts of quicklime with 4000 of water) is poured into this solution, and well mixed by stirring. After standing for about two hours, the liquid is filtered and treated with 1·3% of 30° Bé. caustic soda, and made up to a strength of 17° Bé. The hydrosulphite must be kept cool, and is only stable for a few days. It is used for vatting indigo, indanthrene and algol dyestuffs. Sodium Chloride (common salt) has latterly been recommended for use in dyeing silk with sulphur dyes. Sodium Bisulphite is usually obtained in the form of a 40° Bé. aqueous solution, in which condition it is more stable than in the crystalline condition. The liquid has the suffocating smell of sulphur dioxide. It is occasionally used in silk dyeing, in the preparation of bisulphite and zinc dust vats. Sodium Bicarbonate is a white powder with a bitter, salty, and at the same time alkaline, taste, and is soluble in 9 parts of water at ordinary temperature. It is used for fixing alumina and chrome mordants in silk dyeing. Sodium Nitrate is a friable, crystalline powder, very readily soluble in water, and is used for making nitrous acid in diazotising. Sodium Phosphate is in the form of large, clear, readily efflorescent crystals, with a cooling, salty taste and alkaline reaction. Serves as a fixing agent for stannic chloride in phosphate loading, and as a substitute for bast soap in dyeing loaded silks. Sodium Silicate (water glass) is a clear, colourless or faint yellow, syrupy liquid, with an alkaline reaction. It is used as a fixing or loading agent in the phosphate-silicate process of loading silk. Borax (sodium borate) forms hard, colourless, transparent crystals, soluble in 14 parts of cold, or $\frac{1}{2}$ part of hot, water. Serves as a dye-bath adjunct in dyeing with alkali blue. Sodium Perborate has been recommended as a bleaching agent for Tussah silk. Sodium Tungstate has been recommended for loading silk, for which purpose it is well adapted, but is at present too dear. Sodium Acetate forms large colourless, rhombic columns, which have a cooling, salty taste and dissolve in 3 parts of water. It is used for neutralising strong mineral acids in dye-baths, with the object of replacing such acids by the less powerful acetic acid. Sodium Lactate is a wine-yellow to brownish-yellow liquid of the consistency of thin syrup. Mixed with its equivalent of free lactic acid, it is used, as acid sodium lactate, for protecting the silk fibre against the action of sodium sulphide in dyeing with sulphur dyestuffs. Sodium Sulphide forms large yellowish to greenish, readily soluble lumps, with a strong alkaline reaction and smell of sulphuretted hydrogen.

Calcium Salts.—Of these, calcium acetate is the only one of interest, the crude salt forming the prime material for red mordants, and the pure salt an ingredient in the preparation of aluminium acetate, or an adjunct to dye-baths when the presence of lime in the water is desirable, as, for example, in dyeing Turkey red, alizarine, cœruleine, galleine, galloflavine, dye-woods, etc. For the preparation of nitrate mordants, calcium nitrate finds application.

Magnesium Salts.—The only one of interest is magnesium sulphate (Epsom salts), which is used in loading silk with sugar, and in softening the fibre with cream of tartar.

Aluminium Salts.—In dyeing with certain mordant dyestuffs, the silk must be mordanted with alumina, for which purpose use is made of alum, aluminium sulphate and aluminium acetate. Alum forms large, colourless, crystalline masses, with a vitreous lustre, slightly soluble in cold water, but readily in hot. The aqueous solution has a faint, sweet, astringent taste and a strongly acid reaction. Alum is insoluble in alcohol, and the crystals are slightly efflorescent. Copper vessels must not be used with alum, the metal being soluble in the dissolved salt. For mordanting purposes, alum must first be transformed into the basic condition. Aluminium Sulphate is in shapeless, white masses, soluble in 2 parts of water, but insoluble in alcohol. The aqueous solution has a sweet, astringent taste. For silk dyeing, aluminium sulphate must be free from iron, not more than a faint bluish coloration being formed when 1 grm. of the salt, dissolved in 10 of water, is treated with one drop of tannic acid solution. If a dark blue coloration is produced the sulphate must not be used. This salt also must be transformed into the basic compound before mordanting. Aluminium Acetate enjoys its extensive use on account of the ease with which the alumina it contains can be precipitated on the fibre, whilst the acetic acid volatilises in the warm without harming the material. Owing to this low stability, aluminium acetate is not an article of commerce, but must be freshly prepared for use. There are numerous recipes for this purpose, of which the following can be recommended: One part of aluminium sulphate is dissolved in 2 of water and mixed with a solution of 1 part of calcium acetate in 2 parts of water, the mixture being allowed to settle, and the clear portion taken for use. This solution contains a little lime, which, however, does no harm in dyeing with alizarine.

According to the recipe of the Badische Anilin Co., an aluminium nitro-acetate is prepared, for use as a "nitrate mordant," by separately dissolving 2100 grms. of aluminium sulphate, 555 grms. of calcium acetate and 1350 grms. of calcium nitrate in the requisite quantities of water, and pouring the clear solutions together. To neutralise any iron salts that may be present, the mixture is treated with 3 grms. of potassium ferrocyanide (well dissolved), and then, after standing a short time, with 10 c.c. of 30° Bé. stannic chloride. (*Note.*—The nitrate mordant is not a pure alumina mordant, but a mixed alumina-tin mordant, such as is popular for scarlet and ponceau in silk-dyeing.)

Iron Salts.—Salts of iron are largely used in loading and dyeing silk, and more rarely for mordanting in dyeing with alizarine dyestuffs (chiefly black and reddish-brown). Black mordant (ferrous pyrolignite) is a dark olive-green solution of 12–15° Bé. strength, with a faint smell compounded of acetic acid, smoke and tar, and a faintly acid but inky and astringent taste. It is largely used in loading and black-dyeing. Reddish-brown mordant (basic ferric sulphate) is a dense, brownish-red liquid of sp. gr. 1·35–1·70, and containing 16 % of iron. On dilution with a large volume of water, the solution is decomposed, a more highly basic salt being deposited as a brown sludge, whilst a more acid salt is left in solution. This mordant, also, is largely employed in loading and black-dyeing. Ferrous Sulphate (green vitriol) occurs as dull green, usually damp crystalline masses, dissolving to a pale green solution in water. It is not so extensively used as the other salts mentioned, being mainly confined to the production of logwood, iron blacks and for saddening purposes.

Ferric Nitro-acetate is a deep red solution used in black-dyeing silk intended for plush. The resulting black is stated to stand the hottest pressing and ironing. Ferric Cyano-cyanide, or Berlin blue, is produced on the fibre, this operation constituting the " bluing " process in black-dyeing (*q. v.*).

Chromium Salts.—These salts find only restricted application in silk-dyeing. The following are the most important. Chromium Chloride, which parts with chromium hydroxide more readily than any of the other salts, and is used for mordanting, is met with in commerce as basic chloride : a blackish-green liquid which dissolves to a green solution in water. Chromium Fluoride is a green powder containing 42–43 % of chromic oxide, and is readily soluble in water. It is employed in mordanting, but must not be used in copper vessels, as the hydrofluoric acid liberated during dissociation corrodes the copper extensively. This action can be prevented by an addition of ammonium sulphocyanide. Chrome Alum is in the form of dark violet crystals, soluble in 9 parts of water. The cold-prepared solution turns green when heated above 65° C., but resumes its original violet colour on cooling. It is used for mordanting silk in a bath containing acetic acid. Chrome mordant GA III (chromic chromate) is manufactured by the Farbwerke Höchst. In mordanting silk, the whole of the chromium is easily and completely fixed on the fibre. Chromium acetate forms hard, violet, dusty, dry crystals. It is only occasionally used for mordanting silk, since it yields up chromium hydroxide with difficulty.

Tin Salts.—These compounds play an important part in loading silk, but are only occasionally used in mordanting. The most important is stannic chloride, which was at one time largely made by dyers themselves, by dissolving tin in nitric and hydrochloric acids, and formed a yellow solution known as tin nitrochloride. It is now prepared on a manufacturing scale by oxidising stannous chloride with nitric acid or potassium chlorate. Anhydrous Stannic Chloride is a clear, dense, colourless liquid, of highly corrosive character, which gives off dense white fumes in the air. It has a strong affinity for water, with which it forms a soft, white crystalline and readily soluble mass—the commercial article, $SnCl_4$, $5H_2O$. It keeps well as a concentrated solution, but gradually decomposes if diluted. A solution of 30–35° Bé. strength is used in practice. Stannous Chloride, or tin salt, forms large, clear, pure white crystals, dissolving to a clear solution in a small quantity of water, but exhibiting a slight milky turbidity on dilution, this, however, quickly disappearing on the addition of a little hydrochloric acid. This salt is used in silk-dyeing for cutch black and soft-silk black, in the preparation of stannic chloride, and as an adjunct to alumina mordants for alizarine red. Tin Ammonio-chloride, or pink salt, is a neutral, white crystalline powder, readily soluble in water. It is used for the same purposes as stannic chloride, generally in the form of a 40–45° Bé. solution. Tin Acetate, obtained by mixing stannous chloride and lead acetate (sugar of lead), is sometimes added to aluminium acetate, for obtaining bright shades.

Zinc Salts.—The only zinc salt of importance is the hydrosulphite, which, under the name of "decrolin," is used for stripping colours from the fibre.

Copper Salts.—Copper Sulphate (blue vitriol) forms large, hard, blue crystals, soluble in 5 parts of water. Is not extensively used in silk dyeing, its application being confined to the production of logwood-iron black and cutch brown. Basic Copper Acetate (verdigris) is an amorphous, brilliant green powder, insoluble in water but soluble in acetic acid and dilute nitric acid. Is used in dyeing logwood black. Copper Sulphide serves as a carrier of oxygen in aniline black-dyeing.

Lead Salts.—Lead Acetate (sugar of lead) is not used as such, but is employed in the preparation of aluminium acetate. Basic lead acetate has been recommended for loading white silk.

Antimony Salts.—The only antimony salts to be considered is potassium-antimony tartrate (tartar emetic), a white powder, with a nauseous metallic taste, which acts as an emetic and is soluble in 14–15 parts of cold water, or 2 parts of boiling water. It is used for fixing tannin in after-tanning.

Vanadium chloride and ammonium vanadate are employed as oxygen carriers in aniline-black dyeing.

SOAPS

For our purposes, the commonly accepted meaning of the term "soap" may be extended to include, not merely the fatty-acid compounds of potash and soda, but also those of ammonia, together with the sulpho-fatty-acid salts constituting the Turkey-red oils and "soluble" oils of commerce (monopol soap, monopol oil, tetrapol, etc.). Of the true soaps, in the narrower sense, the only kinds that can be used in silk-dyeing are such as can be readily washed out after use, viz.—

1. *Marseilles Soap.*—This soap is prepared, from the cheaper and inferior qualities of olive oil, in France and Italy (where it is known as Venetian soap). For centuries this class of soap enjoyed the well-merited reputation of being typical of the best quality; but this halo has disappeared. Marseilles has long ceased to produce first-class soaps, and the analyses of Braconnet, Thénard, Bolley and others have shown that the Marseilles soap of the present day is greatly inferior to good tallow curd soap. The name, however, still remains, but no longer implies an olive oil soap made with special care, being applied to any good, salted-out hard curd soap.

2. *Hard Olein Soap.*—This is prepared by saponifying crude oleic acid (stearine oil) with caustic soda. It is yellow-brown in colour, lathers well, and, so long as the water content is small, is very firm. On the average it contains 15–23 % of water, 65–69 % of oleic acid and 6·5–10 % of soda.

3. *Castor Oil Soap* is a hard soap, prepared by saponifying castor oil with the requisite quantity of caustic soda. As a rule it is not salted out, but used in the paste form, and is sold as Turkey-red oil.

4. *Turkey-red Oil.*—The preparation (also known as sulpholeate or alizarine oil), largely used in Turkey-red dyeing, is really nothing but a liquid soap, differing, however, from other soaps by the fact that ammonia forms part of the alkali. Turkey-red oil is mostly produced on a manufacturing scale, the commercial grades being neutral, more or less thick, syrupy, pale yellow liquids, of sp. gr. 1·023. They feel greasy to the touch, but when rubbed between the hands soon reveal the fact that they are not true soaps. They mix with water in all propor-

tions and dissolve therein to strongly frothing solutions with a sharp, bitter flavour and an alkaline after-taste which remains on the tongue for a long time. When rubbed into the skin, they behave exactly like true soaps. Latterly, nearly all commercial Turkey-red oils are made from castor oil. At one time, "tournant" oil, a rancid olive oil, was chiefly used, and later on olive oil, cotton-seed oil and olein, some of which are still employed. The usual Turkey-red oils, however, are sulphoricinolates or sulpholeates of soda or ammonia, or mixtures of both. Preparations of similar composition and action are met with in commerce as para soap, monopol soap (the aqueous solution having a faintly acid reaction), monopol oil, tetrapol, türkon oil, sulphone soap, etc. These "soluble oils" therefore constitute a special class of soaps, which, however, differ from the ordinary commercial soaps in that they do not form insoluble lime and magnesia soaps with hard water.

True soaps are largely used, in silk-dyeing, for scouring, adding to the dye baths, washing, etc., most of the treatments to which the silk is subjected being performed in soap baths. Turkey-red oils and allied substances are chiefly used merely for wetting.

Sundries

Alcohol (spirits of wine) is used, occasionally, for dissolving dyestuffs that are insoluble in water; for example, the spirit-soluble eosines, water blue, indulines and nigrosines.

Hydrogen peroxide, a water-white, colourless liquid, is largely used for bleaching chappe silk and Tussah.

Benzine is a colourless, very volatile and inflammable liquid, with an ethereal smell. It will not mix with water, and is used, in silk-dyeing, solely as a solvent for a limited number of dyestuffs, and for dyeing silk in these solutions (so-called " dry " dyeing).

Glycerine, in the refined state, is a yellowish to colourless, clear, transparent, inodorous liquid, of syrupy consistency and very sweet taste. It is miscible with water and alcohol in all proportions. Is recommended as an adjunct in dissolving sparingly soluble basic dye-stuffs.

Glue.—Commercial gelatine is sometimes used, in tannin-loading, to fix the tannin better.

Albumin, or white of egg, is a loose white powder, readily soluble in water. Serves as a fixing agent in sugar-loading.

Bran, the nitrogenous and fatty husk removed in grinding cereal grains, is used in the form of bran baths, especially in dyeing half-silks, in order to make any of the silk fibres that may have become stained, perfectly white again.

Formaldehyde is usually met with in commerce as a 40 % aqueous solution, or in the concentrated form as a milky gelatinous liquid with a characteristic smell. It is used in the after-treatment of substantive dyeings, in order to increase their fastness to water and washing.

Zinc dust is a fine grey powder consisting of the metallic vapours that condense in the flues of zinc furnaces. It acts as a powerful reducing agent, especially in the presence of alkalis. Is also used in preparing bisulphite and zinc dust vats.

MORDANTING SILK

In order to prepare silk for dyeing with alizarine and other mordant dyestuffs, it must first be mordanted, an operation which consists in the deposition of certain metallic compounds—probably hydroxides—in or upon the fibre. Mordanting is to a certain extent allied to loading, inasmuch as charging the fibre with metallic oxides is naturally accompanied by an increase in weight—that is to say, loading. Only, in mordanting, this loading is merely the means to an end, and not the end itself. How closely the two operations, mordanting and loading, are alike, and how easily each may merge into the other, can be seen from the combined gallnut and iron method of loading, in which the two proceed hand in hand.

In mordanting silk, solutions of metallic salts are used that will readily give up some or all of their contained metallic oxides or hydroxides to the fibre. Some neutral salts dissociate when dissolved; but most of them do not. Most basic salts, on the other hand, give up their hydroxide to the fibre, oftentimes even when the silk is merely immersed in the cold bath. This transfer proceeds the more readily the greater the basicity of the salt. Consequently, when basic salts of this kind are not available, the dyer must prepare the basic solutions himself.

The only metallic salts that come under consideration for mordanting silk, in the true sense of the term, are those of alumina, chrome, iron and (occasionally) tin.

Mordanting with Alumina.—Owing to their high stability, alum and aluminium sulphate are not directly suitable for mordanting, but must first be transformed into the corresponding basic salts or neutralised. This is effected by carefully adding carbonate of soda, in small portions, to the concentrated cold solutions of the above salts, so long as the white flocculent precipitate at first formed continues to redissolve on stirring. When the precipitate will no longer dissolve properly, the addition of the soda is discontinued. For this neutralisation, alum requires the addition of about one-fourth of its own weight of soda crystals. The amount of alum needed in mordanting depends on the depth of the desired shade, and varies from 1 to 15 % of the weight of the silk. The silk is thoroughly wetted and is entered into the cold solution of alum, generally overnight. For pale shades, three to six hours' immersion is sufficient, the silk being afterwards well washed. Neutralising the alum is an operation that requires some degree of patience. If the soda be added too quickly, or in too large quantities at a time, the aluminium hydroxide, which should be deposited on the fibre, will be thrown down prematurely, and wasted so far as the mordanting process is concerned. The neutralisation must be effected in a perfectly cold and concentrated solution of the alum, since the hydroxide will be precipitated from a warm solution, however carefully the soda be added. The mordanting can also be carried on in two stages, the silk being impregnated with a solution of alum at 40–50° C. for two to three hours, equalised on the wringing-post, and then, without rinsing, entered and worked about in a cold bath of bicarbonate of soda for half an hour, after which it is thoroughly washed. When aluminium sulphate (free from iron) is used, 10 parts by weight are dissolved in 50 of water, and to this cold solution is added an equally cold solution of 2–3 parts of soda crystals in 10 of hot water. The addition is made gradually, and gives a clear solution of 8–10° Bé. strength. The silk is entered for four hours, or preferably all night, and is afterwards washed by hand or in the washing-machine.

In all these cases the mordanted and washed silk is worked about for fifteen minutes in a hot bath containing 10 % of soap (based on the weight of the silk), and, after being again rinsed, is ready for dyeing. Occasionally, instead of soaping, the silk is passed through a bath of water glass, to fix the alumina.

In mordanting with aluminium acetate, a solution of 3–5° Bé. strength is prepared, and the silk is allowed to remain in the cold bath for three to five hours, being then taken out and left for a while, and afterwards washed with a little soda, followed by water alone. The procedure is similar in the case of the nitrate mordant, 1–5 % of stannous chloride (tin salt) being added to the aluminium acetate when particularly bright shades (cochineal, scarlet and ponceau) are to be produced. After being rinsed, the silk will be ready for dyeing. The spent mordanting baths can be regenerated with the mordants used.

Mordanting with Chrome.—Chromium chloride is generally used for this purpose, the commercial article, which has a density of 30° Bé., being diluted to 20° Bé., and the well-damped silk entered into the cold bath overnight. For pale shades, three to five hours' immersion will be sufficient, or the bath may be diluted to 3–5° Bé. After a thorough rinsing, the silk should be dyed at once. Sometimes, instead of rinsing, the chrome is fixed by passing the mordanted silk through a 0·5 % bath of bicarbonate of soda, or a ½° Bé. solution of water glass. The spent chrome bath can be made up to its original strength with a fresh quantity of the commercial chloride, and used again. Chrome alum, which is less frequently used, is first neutralised with soda, as in the case of ordinary alum, the resulting basic salt being employed in the same manner as the basic alum. Chromium fluoride is dissolved in water, neutralised with soda, and used like chromium chloride. Both these salts are not very suitable for light shades, the mordanted silk being coloured a fairly strong green. With all chrome mordants the silk must be afterwards rinsed with perfectly soft water, and soaped for two hours in a strong bath of soap at 60° C.

Mordanting with Iron.—In mordanting with iron, for the production of alizarine-iron lakes, basic ferric sulphate alone is used, the strength of the bath being 20–30° Bé. The silk is entered cold overnight, and on the following morning is washed in the machine at 50° C., followed by treatment in a boiling hot, strong soap bath for an hour, and finally rinsed.

Mordanting with Tin.—Tin is generally used, in the form of tin salt or tin acetate, as an adjunct to acetate of alumina, or as stannic chloride in nitrate mordanting, the only instance where tin compounds are used alone being in the production of cochineal scarlet. For this purpose, according to Steinbach, 5 parts of tin filings are dissolved in 12 parts of concentrated hydrochloric acid (free from iron), 3 parts of commercial sulphuric acid being gradually added. Loading with tin is not a mordanting process.

Of other kinds of metallic salts, only those of cerium have been proposed for mordanting silk; and these do not seem to have found any practical application, since their hydroxide readily oxidises in the air, and consequently exercises the same injurious action on the silk fibre as is found in the case of the tin salts used for loading.

Mordanting with Tannins.—Treatment with tannins is not really mordanting, the object of which is to improve the absorptive capacity of the silk fibre for other substances—which is not the case with tannins. It is true that the fibre, and still more the sericin, take up large quantities of tannin and become more or less swollen; but at the same time, charging the silk with tannin lessens its affinity for dyestuffs. On the other hand, silk laden with tannin may be able to take up fairly large amounts of metallic salts, the corresponding tannates being formed. Chief among such salts are the iron compounds, which form with tannin the well-known iron-tannin black, the solid constituent of black writing-ink. This same compound is formed on and in the silk, and thus dyes it black, the silk being entered alternately in the tannin and iron baths until the desired depth of black is attained. With each repetition of the treatment, more iron tannate is formed on the silk, and the weight increases with each bath. This is therefore a regular loading process. In contrast to mordanting with metallic salts, which is effected in cold baths, the tannin baths are used boiling hot, and the silk is entered overnight. If cutch, which gives a green with iron, be used in place of tannin or gallnuts, and the iron salts be replaced by tin salts, stannous catechutannate is formed, which, however, serves merely as a grounding for topping with logwood-iron black. For the foregoing reasons, tannin baths are used subsequent to dyeing, instead of before as in mordanting.

BAST SOAP: ITS PROPERTIES, APPLICATION AND ACTION

As already stated, bast soap is a solution of sericin in Marseilles soap. Since some silks have white bast and others yellow, there are also white and yellow bast soaps, the yellow colouring matter of the raw silk appertaining to the bast and not to the fibre, so that it passes into solution with the bast in the scouring process. Now since, chemically considered, sericin behaves as a weak acid—without, however, giving any decided acid reaction—and since Marseilles soap has an alkaline reaction, the bast soap also has an alkaline reaction. According to the nature of the scoured raw silk and the method of boiling, it is a nearly colourless to yellow, almost clear or milky, liquid, with an alkaline taste and smell, its great defect being that it will keep only a short time.

Bast soap is added in large quantities to the dye baths in silk dyeing, especially in the case of soft silks and écrus. Since it is more particularly used in dyeing with basic, acid and faintly acid dyestuffs, which are always dyed in acid baths, the alkaline reaction of the bast soap would be a hindrance, and it must therefore be neutralised beforehand with sulphuric, acetic or formic acid, and then treated with a sufficient quantity of one or other of these acids to make it decidedly acid to litmus paper or the tongue. The bath is then said to be "soured."

It is desirable to be well acquainted with the real composition of a soured bast soap bath, which is undoubtedly no longer a solution of sericin in Marseilles soap, sericin being insoluble in acids. As a matter of fact the sericin is precipitated in the insoluble form during the neutralisation of the bast soap, and is in a state of very fine suspension in the soured bath. The Marseilles soap, too, is no longer present as such, having been decomposed by the neutralising acid which has combined with the sodium of the soap and liberated the oleic acid. Consequently, the soured bast-soap bath contains suspended sericin, free oleic acid, the sodium salt of the added acid (sulphuric, acetic or formic), and the surplus free acid which produces the acid reaction of the bath. In dyeing, the bath is mixed with a very considerable amount of bast soap, $\frac{1}{4}$ to $\frac{1}{3}$ (by vol.) of bast soap and $\frac{3}{4}$ to $\frac{2}{3}$ of water, in the case of the bast soap from organzine or trame, the proportions being modified to half and half if the bast soap is derived from the treatment of chappe silk. As a rule, however, bast soap from chappe is not looked on with favour, and is only used when better is not available.

Now, the purpose of adding bast soap to the dye bath is not because it facilitates dyeing, for, on the contrary, it makes the finished colours muddy and dull. Since, however, it is always used, there must be some reason in its favour. In finding the explanation it is necessary to make a clear distinction between the dyeing of pure silk, soft and hard silk. The first two kinds still contain a large proportion of the sericin, and hard silk practically the whole. There is therefore the risk of the silk being deprived of more or less of its sericin, that is to say, being partially scoured; and it is to prevent this, or at least minimise it, that bast soap is added to the bath, since a bath charged with bast soap at the outset is naturally less capable of dissolving sericin from the silk than a solution of soap alone. Regarded from this point of view, the addition of bast soap in dyeing soft silk and écru is completely justified. In the case of pure (cuite) silk the conditions are very different, since it contains no sericin, and there is therefore no need to consider the possibility of a loss of sericin in the dye bath, or to add bast soap at all. It is frequently stated in the literature that the employment of bast soap is beneficial to the nature and character of the silk fibre and forms the best means of maintaining the valuable properties of that material. There is no doubt that it does no harm in the case of pure silk; but, on the other hand, no evidence has ever been advanced to show that the omission of bast soap would be injurious to this class of silk. On the contrary, the author and his pupils have made many thousand dyeings on pure silk without bast soap—merely adding acid to the bath—without having been able to discover the slightest injury to the silk fibre. Parallel dyeings with and without bast soap have been made, and the fastness of the resulting colours has been tested, but in no case has any drawback resulted from omitting the bast soap—in fact, the dyeings without it turned out stronger, brighter and cleaner, showing that the livening treatment necessary when bast soap is used can be dispensed with when that ingredient is omitted. It may be objected that acid dyestuffs distribute more evenly when bast soap is used, but this is only true, if at all, in the case of dyestuffs that are difficult to distribute, for which, in order to make sure, a little bast soap may be added to the bath. In any case, however, ordinary Marseilles soap fulfils the same purpose, the sericin having no influence on the distribution of the dye. Silbermann states that sericin has an extraordinary distributing power; but elsewhere he says that the distributing properties of bast soap are "in all probability" due to the presence of sericin. The author's own experience in the subject leads him rather to the view that this action of bast soap—that is to say, the retardation of dyeing—is due more to the soap present than to the sericin. Moreover, uniform dyeing can be obtained, even in the absence of soap, by entering the silk into a lukewarm bath and gradually raising the temperature, beginning with a small quantity of acid and adding the remainder in small portions at a time. It may therefore be concluded that an addition of bast soap is desirable when soft or hard silk is being dyed, but that it is useless in the case of pure silk. Every silk dyer knows that dyeing is actually feasible without bast soap, because it sometimes happens that none is available; and when this is so, Marseilles soap is used. In fact, in dyeing silk loaded with tin, sodium phosphate is used in place of bast soap.

This brings up the question of bast soap substitutes. Bast soap is known to be very unstable, going bad in a few days and giving off a very unpleasant smell. On the other hand, the fact that large quantities of bast soap are used in dyeing soft silk, whereas none is recovered as a by-product, has long been an inducement to look for some substitute. In this connection, preference has been given to gelatine or pale bone glue, Hummel recommending a mixture of: water, 25,000 parts; Marseilles soap, 875 parts; and gelatine, 200 parts; each dissolved separately in water, mixed and treated with 250 parts of olive oil and 30 of caustic soda. Another recipe consists of 50 parts of Marseilles soap and 8 of gelatine, boiled in 2000 of water. Silbermann mentions the following: 1000 parts of Marseilles soap are dissolved in 40,000 of boiling water, and 250–300 parts of glue in 10,000 of water, the two solutions being mixed and raised to boiling, whereupon 130–150 parts of Provence olive oil are added by degrees and stirred in, a short boiling completing the preparation. Ammonium acetate has also been recommended as a substitute for bast soap. Marseilles soap alone is not a complete substitute, especially when the bath is soured, because, in the case of bast soap, this operation liberates the sericin and oleic acid in a state of extremely fine suspension, in which form they remain, forming a true emulsion. Soap, on the other hand, does not form an emulsion when acidified, the fatty acids separating out in drops or lumpy flakes, according to the kind of soap used.

BEHAVIOUR OF SILK TOWARDS DYESTUFFS

In dealing with the loading of silk we have found that silk—and raw silk more than scoured—is able to take up and retain fairly considerable amounts of tannins; and we have also seen that silk does the same in respect of tin when entered into a cold solution of stannic chloride. The process in the two cases is, however, very different, the accumulation of tannin in the silk being purely mechanical, whilst the absorption of tin is a chemical process, the stannic chloride being decomposed by the silk. The best proof of this latter statement is that the bath becomes acid (containing free hydrochloric acid) and poorer in tin. Both phenomena are due to absorption, mechanical in the one case and chemical in the other; and silk exhibits the same phenomena of absorption with regard to dyestuffs. The old controversy of the scientists, whether dyeing is a chemical or a mechanical process, comes up again here; and the answer is that, in some cases, it is purely mechanical, but decidedly chemical in others. When the silk takes up a dyestuff as such, from aqueous solution (that is to say, when the dyestuff is afterwards found in the silk fibre in exactly the same form as it was before), then the case is one of mechanical absorption, the condition being that defined by O. N. Witt as a "solid solution." If, on the other hand, a dyestuff is chemically changed by the silk in dyeing, if the silk takes up only the colour base, or in other cases only the colour acid, of the dyestuff, then the dyeing is a chemical process. Considerations of space preclude further discussion of these theoretical arguments, and it will be sufficient to say that silk has a more or less considerable affinity for all artificial organic dyestuffs, whereas its chemical attraction for the natural dyestuffs is comparatively slight.

The affinity of silk for the various dyestuffs is by no means uniform. For example, fuchsine is taken up, unchanged, from its aqueous solution, at a moderate temperature, without any addition of acid being required. A whole series of acid dyestuffs are absorbed, from aqueous solution, in the cold, on the addition of sulphuric acid; whilst others are only taken up at boiling heat. Thus, in many cases, the temperature is a measure of the degree of affinity—the greater the amount of heat required for the absorption of the dyestuff, the smaller the affinity between the silk and the dyestuff, and vice versa. A second criterion is the time required for the absorption of the dyestuff; some dyestuffs are taken up almost completely in a few minutes, whilst others take hours. A third criterion is the fastness of the resulting dyeing. Generally speaking, in the case of purely mechanical absorption, this is comparatively poor, the mechanically retained dyestuff being removable from the fibre without any great difficulty. For example, the intensive red dyeing given by fuchsine is stripped at once by immersion in alcohol, a proof that fuchsine must have a greater affinity for the latter than for silk. Moreover, that the absorption of fuchsine by silk is solely mechanical is proved by the fact that, when the silk has taken up as much as it is known to be capable of dissolving, it nevertheless continues to take up a further quantity which, however, is no longer dissolved, but is deposited, by surface attraction alone, on the outside of the fibre, the dyestuff retaining its form and colour, *i. e.* with a cantharides-green lustre. So long as the silk appears to be stained red by the fuchsine, the silk is considered to be dyed; but when the green iridescence appears, it is said to be over-dyed. In that case, retaining Witt's definition of a solid solution, we have a super-saturated solid solution. This justifies the assumption that, so long as the silk still appears to be stained red, the dyestuff enters into chemical combination with the silk (presumably combining, to form a salt, with the rosaniline base), whereas the appearance of the green metallic lustre indicates a merely mechanical fixation. Over-dyeing is in all cases something unnatural, just as a super-saturated solution is unnatural.

Silk exhibits a more remarkable affinity for dyestuffs than any other textile fibre, and this is true of all dyestuffs, though the degree of affinity naturally varies. Consequently, for each dyestuff there is a temperature at which its chemical affinity for silk is at the maximum, and at which, therefore, it will give the best dyeing on that material. This fact alone, however, is not sufficient to form a basis for laying down rules for dyeing with the dyestuff in question, other factors having to be taken into consideration. Some dyes, such as fuchsine and a number of basic dyestuffs, are taken up by silk, even from a neutral bath; others, again, *e. g.* alkali blue, require weak alkaline baths; others, again, such as the eosines, phloxines and the substantive dyes, need a weak acid bath; whilst the ponceaus, scarlets and a large number of azo dyestuffs, require strong acid baths; others necessitate the silk being previously mordanted, and then form colour lakes therewith; and finally, some will only dye silk by the vat process. On this purely technical basis, the dyestuffs can be classified, each class corresponding to a specially devised method of dyeing. For instance, the classification could be established on the following lines—

1. Dyestuffs that will dye in a plain neutral bath.
2. Those which dye in a faintly alkaline bath, the weak alkali consisting of soap, soda, or borax.
3. Those which dye in a bast soap or plain bath soured with acetic acid.
4. Those which will dye in a bast soap or plain bath soured with sulphuric or formic acid.
5. Dyestuffs which have to be diazotised and developed on the fibre after dyeing.

6. Those which cannot be used for dyeing until they have been dissolved in sodium sulphide.

7. Dyestuffs which require the silk to be previously mordanted with alumina, chrome or iron salts.

8. Dyestuffs which will only dye after having been reduced by alkali (vat dyestuffs).

The foregoing statements with regard to the behaviour of dyestuffs towards silk only apply, however, so long as silk alone is in question. When a dyestuff is brought into operation on, say, silk and wool, silk and cotton, silk, wool and cotton, or silk and artificial silk, its behaviour undergoes a (sometimes considerable) change. Nevertheless, this point will not be gone into more fully at present, since the opportunity will arise in dealing with the dyeing of wool-silk and half-silk.

The above division of the dyestuff into classes or groups, according to their behaviour in dyeing, has nothing to do with the scientific classification of these substances on the bases of their chemical constitution. With equal justice or freedom they could be classified as fast or fugitive to light, water, washing, milling, boiling, sulphur, soap, etc.; but for purely practical reasons, the foregoing classification according to behaviour in dyeing will be retained in the present work.

Selecting the Dyestuffs and Preparing the Baths

Silk is mostly dyed in bast-soap baths soured with sulphuric acid; and, wherever possible, the dyer will prefer to use this method, provided that the colour or shade he desires can be obtained from dyestuffs capable of being dyed in this way. Shade, however, is not the only requirement to be complied with, the degree of fastness which the customer will expect the colour to possess having also to be taken into consideration. Another point to be borne in mind is whether the silk is pure, soft or hard, and whether loaded or not. Finally, the dyer has to consider whether he can make a profit out of the price he is to be paid for dyeing, if he uses the dyestuffs he thinks necessary for obtaining the results in view. All this entails a certain knowledge of the fastness of the dyestuffs, a subject which is dealt with in special handbooks on the theory and practice of dyeing. When the dyer knows the class of dyestuffs from which he must make his selection in order to obtain the desired fastness, he will also know which method of dyeing has to be employed, and he has then only to fix on the member of that class which he thinks will give the shade he hopes to obtain.

The acid dyestuffs are the class most extensively used in silk dyeing, and especially the acid triphenylmethane group, such as acid green, acid fuchsine, acid violet, etc. They give the brightest dyeings, but have not very strong tinctorial properties—at least in comparison with the basic dyestuffs, which surpass them in intensity, but are, generally, inferior in fastness. As a remedy, the dyer prefers to combine the use of acid and basic dyestuffs wherever possible.

The substantive dyestuffs, which are employed in a bast-soap bath soured with acetic acid, are also largely used. They have a high affinity for silk, draw quickly, and, for the most part, completely, and the majority give dyeings that will stand water.

Mordant dyestuffs furnish dyeings that are perfectly fast to milling, and in most cases to light as well. The dyeing process is, however, troublesome, since the silk must first be mordanted, then rinsed and afterwards dyed. As a rule they are only used when dyestuffs of equal fastness are not available in other classes.

Sulphur dyes are regarded by the silk dyer with a certain amount of distrust, fearing—not without reason—the injurious action of the strongly alkaline sodium sulphide on the silk. Moreover, there is no pressing reason for employing these dyestuffs, the other classes already mentioned providing all shades and of any desired fastness.

Vat dyestuffs have not hitherto been much used for silk, because the caustic soda in the bath is by no means beneficial, especially in warm dyeing. On the other hand, these dyestuffs give colours of unsurpassable fastness.

After deciding on the method of dyeing, the next step is the preparation of the bath. The first point to be considered is the bath ratio, or the relative weights of water and soap to be taken. Each kind of fibre requires a definite amount of water for dyeing, that is to say, enough to allow the material to be worked about conveniently; but not such an excess as will render the dye liquor unnecessarily dilute. For silk, the most suitable quantity of water is found to be about thirty times the weight of the silk, though it may be increased to forty or fifty times if bast soap is to be omitted. With bast soap, however, it is undesirable to go beyond 1 : 30; otherwise an excessive quantity of this latter ingredient would be required. That soft water (free from lime) must be used has already been emphasised. The dye vats are preferably made of copper. If wood is selected, it is advisable to line the vats with jute cloth, to prevent the tender silk from catching on splinters and tearing. The bath is heated with direct or, preferably, indirect steam, the former soon making the liquor too dilute.

Any additions, such as bast soap, acids, salts and the like, must be added before the dyestuff, and care must be taken to see that they are properly dissolved or well mixed. Special care is necessary in dissolving the dyestuff, which operation should never be performed in the bath, but separately, and preferably with distilled (or condensed) water at boiling heat. As an additional precaution, the dyestuff solution should be poured through a hair sieve into the bath—usually in successive portions—the mixture being finally well stirred. In some dyeworks it is customary to boil the bath up once before the silk is entered, but when this is done, the bath must be carefully re-cooled, since only medium temperatures (50–80° C.) are required for dyeing silk. The boiling and re-cooling are therefore only a waste of time. The best plan is to enter the silk and work it several times in the bath, before the dyestuff is added. The author does not recommend the practice of boiling the bath up again every time fresh dyestuff is added—at least this should not become a habit. In most cases a temperature of 60–80° C. will be amply sufficient in dyeing, though in the case of chappe silk, boiling is more in place.

The silk must be carefully wetted before entering the bath, this being essential to the success of the subsequent operations. Silk being a porous material, contains large quantities of air which must be expelled by wetting; and since this air is obstinately retained, hot water must be used, the wetted silk being preferably well squeezed and then wetted again. Insufficiently wetted silk, still containing air, will remain undyed at the points where the air bubbles occur, the dyed silk being then covered with pure white spots which are entirely due to imperfect wetting. For these reasons, the importance of careful wetting cannot be over-emphasised.

In no branch of dyeing is there so strict a line of demarcation as in the case of silk On the one hand is the black-dyeing industry, the chief ambition of which is to produce nothing but black, in all imaginable shades and in the greatest perfection, or—where required—as cheaply as possible. On the other hand, the colour dyer produces all colours except black.

Dyeing with Basic Dyestuffs

Dissolving basic dyestuffs is an operation entailing a certain amount of care, many of them when dissolved or suffused with hot water (methyl violet in particular) having a tendency to "ball," whilst when mixed with a small quantity of water, they form tarry or resinous lumps which stubbornly resist further attempts to dissolve them. This is a disagreeable property of basic dyestuffs, but can be circumvented by stirring up the dyestuff with cold water, adding a few drops of acetic acid and then bringing into solution with warm water. The less readily soluble dyestuffs, such as fuchsine in crystals, however, require hot water to bring them into solution; and if they become lumpy, the only remedy is filtration. Such as are very difficult to dissolve should be stirred with their own weight of glycerine and a fourfold quantity of alcohol, then warmed on the water bath, and the resulting syrup dissolved in hot water. The basic dyestuffs are among the oldest artificial organic dyestuffs known. Most of them are distinguished for the brilliancy and intensity of their dyeings, foremost in this respect being the basic triphenylmethane dyestuffs, especially methyl violet, malachite green, brilliant green and fuchsine. In spite of their beautiful colour, however, the fastness of these dyestuffs, particularly towards light, is only moderate, so that, notwithstanding their beauty and low price, they have been displaced by faster dyestuffs where this quality is a consideration. Consequently, their employment in silk dyeing is restricted to dyeings in which a high degree of fastness is not required, or for shades which, at present, can only be obtained in their full beauty by the use of basic dyestuffs, such as the rhodamines. Fuchsine finds the largest application of any. It is rather difficult to dissolve, especially when in large crystals, mere suffusion with hot water being frequently insufficient to bring it into solution. If any of the dyestuff remains undissolved, it must be warmed, together with the solvent, until the desired result is obtained. When fuchsine crystals are used, the high purity of the commercial article enables pouring through a sieve to be dispensed with. Fuchsine has a high tendency to overdye silk, particularly when the dye bath contains lime. It also readily deposits as small crystals when the bath cools down, to prevent which the liquor must always be kept at about 80°; and it is also advisable to add a little acetic acid and alcohol.

All the basic dyestuffs have a decided affinity for silk fibre, which will take them up from their neutral solutions in water, without any further additions, at a moderate temperature. In practice, however, the conservative tendencies of the dyer have mostly led to the retention of the soured bast-soap bath, because, in many instances, he fails to realise the fact that silk can be dyed without bast soap. Even when experience has shown that this can be done, he feels doubt about the fastness of the dyeing, although it has been proved that this is not a whit better with bast soap than it is without. In the opinion of the dyer, bast soap belongs to the dye bath with just as much right as bast to silk; but, in the former case, the right is merely one established by custom.

Experience has also shown that there is no need to sour the bast-soap bath with acetic acid when dyeing with basic dyestuffs; and the acid, at least, could be saved, even though the luxury of bast soap may be indulged in when this material is available in sufficient quantity. These remarks, of course, apply solely to cuite silk, as souples and écrus must be dyed with bast soap. Now, it is a common practice to dye fuchsine in a neutral (unsoured) bast-soap bath; but with all the other basic dyestuffs, soured baths are used, because "it is always done in practice!"—a remarkably unpractical practice! Nevertheless, it must be admitted that a few basic dyestuffs actually require the addition of acetic acid to the dye bath, such as methylene blue, new methylene blue, rhodamine scarlet, rhoduline orange and auramine; and this acid is also used in dyeing loaded silks, on which the basic dyestuffs generally give fuller shades than on unloaded silk. In view of the great affinity of these dyestuffs for the silk fibre, it is inadvisable to add the whole of the dyestuff to the bath at once, the better plan being to run the solution in in small quantities, waiting in each case until the previous portion has been absorbed by the material. If the bath is soured, an excess of acid should be avoided as hindering or retarding the absorption of the dyestuff. On the other hand, this retardation is beneficial in the case of dyestuffs that equalise with difficulty, since it helps to secure greater uniformity. Victoria blue B, however, forms the exception to this rule, as it will stand not only acetic acid in excess, but even sulphuric acid. This dyestuff lies, as it were, on the border line between the basic and acid dyestuffs, and its peculiar behaviour is attributable to its chemical constitution. The same applies to the cotton-blue marks.

The great affinity of the basic dyestuffs makes it unnecessary to warm the bath to 80–100° C., as is sometimes advised, the only case in which a high temperature is required being fuchsine, which is difficult to dissolve. As a rule, 65° C. will be high enough, rising to 80° in the case of fuchsine. The best plan is to enter the silk into the lukewarm bath, working it about well and adding the dyestuff by degrees, but not beginning to raise the temperature (gradually) until the dyestuff is all in. The dyeing will be completed in about three-quarters of an hour, in many cases even sooner. The end of the operation can be recognised from the bath becoming nearly or quite exhausted of dyestuff. With chappe silk, the bath can be heated nearly to boiling point, because the material is firmly twisted and consequently does not take up the dyestuff so easily.

The dye-bath can, of course, be used over again. In this connection, attention may be drawn to a peculiar feature in the conditions of affinity exhibited by certain dyestuffs. For instance, some dyestuffs that are taken up by the silk at a medium temperature will strip at a higher one, whilst others added when the bath is boiling are not absorbed until it has cooled down. This circumstance accounts for the rule that, when dyeing to pattern, the silk should be lifted from the bath the moment the desired shade is attained.

In general, the basic dyestuffs are not well adapted for use in combination with others of the same group, proper distribution being difficult, and sometimes impossible, to secure in these circumstances. For instance, auramine and methyl violet cannot be combined, being mutually antagonistic. On the other hand, the material may be grounded with one dyestuff and topped with the other, in which case the dyeing will exhibit the shade of the combination when viewed by transmitted light, but principally that of the topping colour by reflected light.

If several basic dyestuffs are to be used in combination, a selection must be made of such as will dye at the same temperature. In this respect, they are by no means all alike, some absorbing better at a high temperature, others at a low. On this account it may happen that different parcels of material dyed with the same proportions of dyestuffs may vary in shade, according to the temperatures employed.

The basic dyestuffs will not stand the action of water, and therefore must not be used for umbrella silks. To improve the dyeings in this respect an after-treatment with tartar emetic and tannin is necessary. The first stage is to treat the dyed material with 4 % of tannin for an hour at 30° C., and then, without any intermediate rinsing, for half an hour with 2 % of tartar emetic in the cold, followed by a thorough rinsing. Sometimes the tartar emetic is omitted, the material being treated for one to two hours in cold or lukewarm water containing 0·2 % of tannin. An after-treatment of this kind, however, more or less affects the original shade.

The fastness of basic dyestuffs to light is less than could be desired, only methylene blue and Capri blue being really fast. Moreover, this property is more or less affected—either improved or impaired—by loading, but not in accordance with any definite rule or degree of regularity. In some cases it can be improved by coppering, the dyed material being treated with 1–3 % of copper sulphate and a little acetic acid for fifteen to twenty minutes at 50–60° C. This, however, affects the shade more or less, by rendering it duller, which is possibly the reason why the method has not made any headway in practice, though the dyeings are much faster to light.

When the dyeing process is completed, the colour is brightened with dilute acetic or tartaric acid (15 parts to 100,000 of water), the material being then rinsed and dried. Sulphuric acid is not suitable for this final treatment, having an unfavourable effect on many basic dyestuffs. If no bast soap has been used in the dye-bath, the brightening treatment can be omitted.

The basic dyestuffs are less frequently used alone than in combination with members of other groups; for example, acid, faintly acid and even substantive dyestuffs. Since basic and acid dyestuffs not infrequently precipitate each other, they naturally cannot be used together in the same bath. Either the material is dyed first with the acid dyestuff, well rinsed and then topped with the basic dyestuff in a second bath, in order to make the colour richer and brighter, or the above order is reversed. Since, in many cases of this kind, there appears to be some chemical combination formed between the two classes of dyestuff, the fastness of the colours is improved.

The basic dyestuffs are employed in a similar manner to increase the beauty of logwood-black dyeings by shading.

Dyeing with Acid Dyestuffs

No method of dyeing on silk is so frequently practised as that in which acid dyestuffs are used in a bast-soap bath soured with sulphuric acid, 80–90 % of the coloured dyeings (excluding black) being obtained by this method. So firmly is it established and retained that Steinbeck, in his work on dyeing, advised the dyestuff manufacturers that, in offering new dyestuffs for silk dyeing, the main point to consider was that all dyestuffs recommended to silk dyers should be suitable for dyeing in a soured bast-soap bath along with the dyestuffs in common use.

It is a fact that, wherever practicable, the silk dyer prefers to use a bast-soap bath soured with sulphuric acid, and that he only departs from this custom under stress of circumstances, either because the acid dyestuffs available will not give sufficiently fast colours, or because his customer has expressly stipulated some other method.

The bath is prepared by mixing 1 part of bast soap with 2 of water, and adding dilute sulphuric acid until the bath has a decidedly acid reaction or taste. It should be noted that loaded silk requires more acid in the dye bath than unloaded. The dyestuff is added in a properly dissolved condition, and, preferably, filtered. The silk being entered into the lukewarm bath, must be constantly worked about, and the bath temperature gradually raised to 80° C., an increase to boiling heat being seldom required. The dyed material is well rinsed, and brightened in water containing 5 % of sulphuric acid.

The use of bast soap is not unconditionally essential, it being possible to dye silk in a bath containing sulphuric acid alone, without fear of uneven dyeing, provided the dyestuff solution is added in small portions and the liquor only gently warmed, or when dyestuffs that distribute well are used. The addition of Glauber salt to the bath is not to be recommended. The omission of sulphuric acid from the bast-soap bath would result in the silk not being dyed at all, bast soap in itself directly retarding the absorption of the dyestuff. This explains why the addition of bast soap to the acid bath protracts the dyeing process and acts as a kind of regulator, a more gradual absorption of the dyestuff being obtained by increasing the proportion of bast soap, and the contrary effect by using more acid. The bath temperature forms a second regulator. It is not generally known that silk can also be dyed in the cold with acid dyestuffs, when plenty of time can be allowed. Since the higher the temperature the quicker the absorption, the dyeing can be completely controlled, and either accelerated or retarded as desired. The omission of the bast soap seems more particularly advisable in the case of light colours, owing to the danger of the shade being affected by the yellow colouring matter of the sericin passing into the material. The usual temperature with acid dyestuffs is 70–80° C., though lower temperatures can be employed if more time is given. In any event the bath should be at hand temperature when the silk is entered, and then warmed up slowly. The cold process is more particularly used in matching difficult shades, the temperature being slowly raised only after the desired match has been obtained. In no event must the bath be allowed to boil, for even when a high temperature is necessary, the dyeing can be completed below boiling heat.

Nearly all the acid dyestuffs are suitable for silk, provided the material consists of silk only. The conditions are different when wool and silk are present in the same bath. At present, however, we are not concerned with these conditions, as we are now dealing with silk alone. Speaking generally, it may be said that any acid dyestuff which will dye wool is also applicable to silk; and there are a few others which are used almost exclusively for silk, being too expensive for wool, *e. g.* silk scarlet, phœnix red, naphthyl blue and silk blue.

In view of the very large number of the acid dyestuffs and of the fact that the method of dyeing is the one most extensively pursued, the subject will be dealt with in greater detail. Naturally, it is out of the question to give a list of all the acid dyestuffs, or to describe them, and we must restrict ourselves to a general summary.

The acid dyestuffs may be divided into two main groups : those which distribute easily, and those which do not. By distributing is meant that the dyestuffs produce uniform and homogeneous dyeings at temperatures approaching boiling point ; that is to say, dyeings that are free from inequalities, irregularities, parti-coloured, spotty or cloudy patches. The dyestuffs belonging to this category have a second valuable property, viz. they can be used jointly in all proportions and even then, in all circumstances, furnish uniform dyeings in which the individual components are completely merged into one another and can no longer be distinguished, as such, in the mixture. Owing to their relatively low affinity for the silk fibre, the distributing dyes can safely be used without bast soap ; and, on the other hand, they will stand high temperatures—indeed some of them are not absorbed unless the temperature is high. The omission of bast soap applies, of course, only to pure silk, for soft and hard silks must be dyed in a soured bast-soap bath.

The non-distributing (" uni ") dyestuffs do not give uniform dyeings under the same conditions as the other group, and in order to obtain good dyeings on silk with this extensive series, the method of dyeing must be modified accordingly. They differ principally from the distributing dyestuffs in their much greater affinity for silk, so that they dye this material with comparative ease and rapidity, the absorption being good and often complete. In consequence of this rapid absorption, however, the resulting dyeings are mostly uneven, and as the dyestuff does not penetrate into the interior of the fibre so well, but remains more on the surface, it is liable to rub off. All these unwelcome features are accentuated when a strongly acid bath is used, the affinity diminishing with the acidity and temperature of the bath. Consequently several divergent methods of dyeing are employed.

1. The bath is prepared, in any case, with bast soap, but is soured with acetic acid instead of sulphuric acid.

2. The silk is entered in the unsoured bast-soap bath and worked about, the requisite amount of sulphuric acid being diluted and added in small successive portions while dyeing proceeds.

3. The silk is entered into the cold bast-soap bath (soured with acetic acid), the temperature being then raised to 50° C., and a little sulphuric acid carefully added, to help the absorption of the dyestuff.

Whereas in dyeing with distributing dyestuffs, the baths are mostly not exhausted, considerable quantities of dyestuff being left behind, the baths of the non-distributing dyestuffs are usually quite spent. Of course, the line of demarcation between these two groups of dyestuffs is not sharply defined; the less completely the dyestuff draws, the more decidedly does it belong to the distributing group, and the more completely, the more readily is identifiable as belonging to the non-distributing class. In fact, some acid dyestuffs are so close to the border line that they are classed with one or the other group according to individual predilection. There exists, however, another characteristic difference between the two groups, viz. that the non-distributing dyestuffs cannot be used in combination with one another, since they then give, instead of a properly blended shade, parti-coloured and chequered dyeings which are of no practical value. In the most favourable circumstances, dark Russian green, dark Bordeaux red or dark brown are the only shades obtainable by combining the dyestuffs of this group, because the unevenness of the dyeing is difficult to detect in these dark shades. Hence, when combination dyeings have to be made with acid dyestuffs, the distributing kinds must always be used, being dyed in a bast-soap bath soured with sulphuric acid, or in a plain bath forming a weak solution of the same acid. The non-distributing dyestuffs are nevertheless largely used, though always singly. Neither should members of these two groups of acid dyestuffs be used in combination.

In combined dyeings with distributing dyestuffs, care should be taken to select such as are as nearly as possible equal in point of fastness. There is really no object in combining a dye that is fast to light with one that is fugitive, since the latter would gradually fade and the dyed shade change colour accordingly. Consequently, dyestuffs fast to light, milling, etc., as the case may be, must be used together. In order to obtain uniform shades from such combinations, the component dyestuffs must be used concurrently, and not in succession, as, in the latter event, the dyestuff last used would top and mask the ground colour.

The acid dyestuffs are not fast to either washing, milling or the action of water, and therefore when shades possessing these properties are required, acid dyestuffs must be abandoned in favour of substantive or mordant dyestuffs. On the other hand, there are plenty of acid dyestuffs that are very fast to light, so that there is no difficulty in this respect. The most fugitive are the acid triphenylmethane series obtained by sulphonating the corresponding basic dyestuffs, this treatment greatly reducing the fastness and tinctorial power. At the other end of the scale, the class of acid azo dyestuffs include a large number of valuable members fast to light, such as ; azofuchsine, azo-eosine, crocein-orange G, fast yellow extra, fast pale yellow, cupramine yellow, fast wool blue, Victoria black, etc. The most interesting in this connection, however, are the members of a small group of alizarine dyestuffs, which dye in a strongly acid bath, distribute excellently, and give dyeings that are fast to light: *e. g.* alizarine rubinol, alizarine irisol; whereas alizarine cyanine green, alizarine emeraldol and alizarine pure blue do not distribute so well, and alizarine saphirol, although it distributes perfectly, is somewhat inferior to the others as regards fastness to light.

Since the acid dyestuffs in general have not any great covering power, whilst the employment of large quantities tends to cause bronzing, the tendency of dyers is to top them with basic dyestuffs, this making the shade richer.

To improve the fastness to water, the same after-treatment with tannin as is employed with basic dyestuffs can be given; but as the acid dyestuffs do not form any lakes with tannin, the latter must be fixed with tartar emetic. After-treatment with aluminium acetate seems to be little practised, for though it produces the desired effect, it makes the silk softer than is desired.

A brief description will now be given of the various shades which can be produced from acid dyestuffs by the methods described above.

Red.[1]—Azo-fuchsine G and alizarine rubinol marks are preferred among the distributing dyestuffs on account of their fastness to light. Azo-eosine and brilliant croceine

---

[1] Most of the dyestuffs mentioned below are manufactured by the Farbenfabriken Bayer, the author's long connection with the firm having made him most familiar with their products. It being impossible to specify all the dyestuffs that can be used, those mentioned are merely given as typical. Of course, other makes of similar dyestuffs could be used just as well, and full information on these dyestuffs is given in the publications issued by the different firms.

3B are fast to light, but do not distribute so well. Of the fugitive reds, fast red A is the one most largely used, together with the marks: ponceau R, 2R, 3R, silk scarlet and some of the cloth reds, which are specially suitable for unloaded silks.

Orange.—Orange II is largely used as a distributing dyestuff, and croceine orange G and fast light orange G on account of their fastness to light.

Yellow.—The fast pale yellow marks are distinguished by their distributing properties and fastness to light. Indian yellow and the tartrazines (which are fast to light and in part distribute well) are also popular. On account of their clear greenish tinge, the quinoline yellow marks, KT extra in particular, are employed. Fast yellow extra is the most suitable for unloaded silks.

Green.—The greens that distribute well are only absorbed with difficulty by silk, brilliant acid green 6B being the best in this respect. Alizarine cyanine green and alizarine emeraldol are used on account of their excellent fastness to light, but they both distribute with difficulty, and are therefore best dyed with acetic acid. Bright green shades on silk are best obtained with fast pale yellow or quinoline yellow, in combination with wool blue or brilliant acid blue.

Blue.—The number of blue acid dyestuffs is particularly large, alkali blue being extensively used because the dyeings are uniform and fast to light, water and milling. Alkali blue is dyed like the basic dyestuffs, in a neutral or faintly alkaline soap bath, sometimes also with sodium phosphate or borax, the blue being developed in a fresh warm bath containing sulphuric acid. Victoria blue is also used in place of alkali blue, but is dyed in an acid bath. Other popular dyestuffs are the old water blue, silk blue, methyl blue for silk, cotton blue, navy blue, light blue, pure blue for silk, night blue (superfine), opal blue (conc. X). A few of the indulines are specially suitable for silk, *e. g.* silk-induline (Kalle). Sometimes alkali blue is used for grounding, being topped with a suitable induline. Bleu fluorescent (Sandoz) and naphthyl blue (Kalle) are favoured for fluorescene blue shades. Alizarine pure blue and the fast wool blues are very fast to light, but do not distribute well.

Violet.—Acid dyestuffs are not much used for violet shades, the basic violets being preferred. For very fast dyeings, violamine (Höchst) is employed, and very strong dyeings that are also fast to light are obtained with Victoria fast violet. Among the older violets in use are alkali violet and fast acid violet 10B.

Brown.—There are no brown acid dyestuffs suitable for silk.

Black.—Though there are many black acid dyestuffs, they are rarely used for silk, nearly all the blacks being obtained with logwood. It is true that silk can be dyed black with acid dyestuffs, but the process is too expensive, the quantity of dyestuff required being so large (12–15 %) that the black cannot compete with logwood. The most suitable are naphthalene acid black 4B, and for unloaded silks, naphthylamine black 4BL, whilst the sulphoncyanine black marks are applicable to both loaded and unloaded silks.

Weak Acid Dyestuffs.—These form a small group, usually dyed in a bast-soap bath slightly soured with acetic acid. They are also known as eosines, resorcine dyestuffs and phthaleine dyestuffs. The division is a purely arbitrary one, because there are many other acid dyestuffs that can also be dyed in an acetic soap bath, and which might, with equal justice, be included in the "weak acid" class.

The group comprises the eosines, phloxines, erythrosines, rhodamines and rose bengale dyestuffs. The rhodamines are really basic dyestuffs, but can also be dyed in acetic, and even sulphuric, bast-soap baths. The members of the group are largely employed, owing to their brilliance, and in some cases also on account of their peculiar fluorescence. They are readily absorbed, and distribute well enough in presence of a sufficiency of bast soap, but are very fugitive to light (the rhodamines being the best), nor are they suitable for combining with other acid dyestuffs. When the dyeing is completed, the colours are livened in a bath containing 10 parts of acetic acid or 5 of tartaric acid (instead of sulphuric acid) in 2000 parts of water. The bast-soap bath may contain 5–10 % of ammonium acetate instead of being soured with acetic acid; and the fastness to water can be improved by an after-treatment with tannin.

Dyeing with Substantive Dyestuffs

The substantive dyestuffs are not, even now, employed to the extent they deserve. For silk, they are equal, if not superior, to the acid dyestuffs in tinctorial value. Their chemical affinity for silk is very considerable; they absorb well, and often completely; the resulting dyeings are, on the whole, faster than those with acid dyestuffs. On unloaded silk, most of them are fast to water, and though they are less so on loaded silk, they can be improved by after-treatment with tannin. A large number of the substantive dyestuffs are fast to light, and some of them are fast to washing and milling; that is to say, they are adapted to satisfy more stringent requirements in respect of fastness than the acid dyestuffs. They have, however, one defect, at least in the eyes of the average silk dyer, viz. that they cannot be used in a bast-soap bath soured with sulphuric acid, because they absorb too quickly and then give uneven dyeings. The extreme conservatism of the silk dyer is only too well known; but it is very foolish to reject dyestuffs possessing such excellent properties solely because they do not fit in well with his usual methods of working. The substantive dyestuffs, also known as benzidine or diamine dyestuffs, are, moreover, cheap and give rich dyeings. They can also be topped with basic dyestuffs, with which they form very fast, lake-like compounds that are sufficiently fast to water; so that, even if the individual dyestuffs of this group have a low covering power, they can be helped out by topping with a basic dyestuff.

The substantive dyestuffs dye best in a bast-soap bath soured with acetic acid, 2–5 % of the acid being taken according to the amount of dyestuff used, whilst, for very deep dyeings, the quantity of acid may be increased up to 10 %. To obtain gradual and uniform absorption, it is advisable to add the acid in successive portions, and not all at once. One maker's recipe prescribes, in place of the bast-soap bath, a bath containing 10–20 % of Glauber salt crystals and 1–2 % of acetic acid. The author, however, cannot recommend this method, because saline solutions are not good for the silk fibre and should be excluded. It would be preferable to dye in a neutral bath of ammonium acetate, without bast soap. This salt, which is non-crystalline, is gradually dissociated at high temperatures, a little ammonia being set free and the bath becoming progressively richer in acetic acid as dyeing proceeds, thus securing a more gradual and uniform absorption of the dyestuff. It is generally recommended that the bath should be raised to 90° C. and kept for an hour at that temperature; but, though this applies to a number of acid dyestuffs, it is not suitable for all, the majority dyeing best between 60 and 80° C.

Weak alkalis oppose or retard the absorption of substantive dyestuffs by the fibre, and therefore a bath of bast soap alone is unsuitable, being always alkaline. The alkali must therefore be neutralised until it gives a faintly acid reaction except in the case of those members that are very sensitive to acid, such as congo and benzopurpurine 4B. On the other hand, those fast to acid will stand a large addition of acetic acid, and on the whole the substantive dyestuffs absorb better from slightly acid baths than from neutral liquors. The affinity of these dyestuffs for silk varies to some extent, the greatest being exhibited by those, such as deltapurpurine 7B, diamine scarlet B and 3B, congo orange, and chrysophenine, which will dye silk in a plain bath without acetic acid. Then come those, such as benzopurpurine B, rosazurine B and G, diamine yellow N and diamine green B, which require only a small addition of acetic acid. The slighter the affinity, the larger the quantity of acetic acid needed to force the dyestuff on to the fibre. This last category includes, for example, Mikado orange, Mikado yellow, curcumine S, direct yellow, R and diamine golden yellow, which can be dyed in nearly the same way as acid dyestuffs.

In dyeing pure silk, the bast-soap bath can, of course, be omitted, and the operation conducted in a plain bath with acetic acid, the distributing power being by no means so low as is frequently stated. Sufficiently even dyeings can be obtained by entering in a slightly soured plain bath at lukewarm temperature and gradually warming up. The dye-baths can be used over again. The after-treatments usually applied in the case of cotton, such as chroming, coppering and the like, are not practised in silk dyeing. Improving the fastness to water by an after-treatment with formaldehyde would probably be in place with such dyestuffs as do not give sufficient fastness in the ordinary way.

Red.—The red substantive dyestuffs are so numerous that it would be impossible to specify them in detail. As there are now many reds that are fast to acids on the market, the sensitive reds are discarded. Among those fast to water are: benzo fast red GL, benzo fast scarlet 4FB and 8FB, benzo red 10B; fast to light: benzo light red, benzo light ruby, benzo light Bordeaux. The benzopurpurine marks are not suitable for loaded silks.

Orange.—Toluylene fast orange LX is fast to both water and light. Others fast to light are: benzo light orange, benzo fast orange and Pluto orange.

Yellow.—The most important is chrysophenine, on account of its fastness to light and, particularly, water. Chrysamine and chloramine yellow GG and HW are also fast to water.

Green.—The substantive group also contains greens, but they are not sufficiently bright, and none of them is fast to light. On the other hand, benzo dark green, benzo green and benzo olive are fast to water. The basic greens are preferred owing to their superior brightness, or the silk is bottomed with substantive dyestuffs and topped with a basic green.

Blue.—These dyes play an unimportant part at present, their chief use being for dyeing half-silks. They cannot compete in price with the cheap water blue and alkali blue, and moreover are tinctorially inferior to the sulphone cyanines and sulphone azurines; they are absorbed with difficulty as a rule, and require a comparatively large amount of acetic acid. If, however, it is desired to use substantive blues, the following can be recommended as fast to water: brilliant azurine 5G and brilliant fast blue B and 3BX; and as fast to light, benzo fast blue and brilliant fast blue.

Violet.—Substantive dyestuffs are little used for violet on silk. The most important, as being fast to both water and light, are brilliant benzo fast violet 4BL and 5RH.

Brown.—Here again, substantive dyestuffs are not much used, the best (as being fast to light and water) being: benzo brown CB and 3GC, benzo chrome brown B, G and R, and toluylene fast brown 2R.

Black.—The substantive blacks are used only for half-silks, with the exception of diazotised black, which will be dealt with in the next section.

DYEING WITH DIAZOTISED DYESTUFFS

All the diazotised dyestuffs belong to the substantive group, and therefore all that has been said with regard to these dyestuffs and their manner of application applies to the former also. In the majority of instances, however, the dyeings obtained direct are not sufficiently fast to be usable in that condition. Nevertheless, they can be converted into fast dyeings—provided the dyestuff contains free amido groups—by diazotising, followed by developing or coupling. The chemical reactions and method of procedure are just the same as in the case of cotton.

In practice, the diazotising is effected in the following manner:—

The dyed and rinsed silk is entered at once into the cold diazotising bath and is worked about constantly for fifteen to thirty minutes. For each 100 parts of silk the bath contains 3 parts of sodium nitrite dissolved in 1500–2000 parts of cold water, 8–10 parts of crude hydrochloric acid (20° Bé.) being added. The operation must be conducted in wooden vats, metal vessels or fittings (lead excepted) being unsuitable. At one time, ice was used for cooling during the process, but this has been given up in favour of water at ordinary temperature, and in some cases, *e. g.* diazo indigo blue, the bath may be allowed to rise to 20–30° C. As a rule the diazotisation will be complete in fifteen minutes, though some dyestuffs take longer and have to be left in the nitrite bath for half an hour. The goods are centrifuged or squeezed, contact with metal being avoided. A lead-lined hydro-extractor may be used, or else the goods must be wrapped in packing-cloth.

The intermediate diazo compound formed on the fibre is very unstable and sensitive to light, especially direct sunlight. The operation must therefore be carried on in a shady room, and care be taken to prevent any part of the diazotised goods from getting dry, or streaks and spots will be formed in the coupling stage. The diazotised material is rinsed and then immediately entered in the developing bath. The nitrite baths will keep for a considerable time, and can be freshened up for use by the addition of one-third the original amounts of nitrite and acid. During the whole process the bath should smell strongly of nitrous acid. In the case of light shades the bath may be weaker in nitrite and acid.

The developing baths are prepared in the following manner, for the various developing agents specified :—

β-Naphthol.—For 10,000 parts by weight of silk, 50–100 parts of β-naphthol are dissolved in 41–82 parts of caustic soda (40° Bé.) and diluted with 150/200,000 parts of water. The silk is worked about in the bath for twenty to twenty-five minutes, then rinsed and lightly soaped. For use over again, the bath is replenished by the addition of 35–70 parts of β-naphthol and 30–60 of caustic soda. An excess of alkali should be avoided as injurious.

Sodium β-Naphthol: Developer A.—For the above weight of silk, 100–200 parts of developer A and 50 of sodium carbonate are dissolved in 150/200,000 parts of water at 30–35° C. The bath is used as above.

Resorcine: Developer F.—The bath consists of 70 parts of resorcine, dissolved in 140 parts of caustic soda (40° Bé.), and 150/200,000 parts of water.

Phenol.—The above quantity of bath liquor contains 40 parts of phenol dissolved in 80 of caustic soda.

Meta-Toluylenediamine Hydrochloride: Developer H.—50–75 parts of this preparation are dissolved with 15–20 parts of sodium carbonate in 150/200,000 of water.

Ethyl-β-Naphthylamine: Naphthylamine Ether: Developer B.—The bath consists of the above quantity of cold water, to which are added 100–125 parts of the preparation dissolved in 30,000 parts of hot water and a little hydrochloric acid.

Amidodiphenylamine: Fast Blue Developer AD.—270 parts of this developer are dissolved in 2000 parts of boiling water, 35 parts of hydrochloric acid, and the whole diluted to 150/200,000 parts.

Amidonaphtholsulphonic Acid G: Blue Developer AN.—175 parts of the preparation are suffused with 2000 parts of cold water. After frothing has subsided, 5/10,000 parts of water are added, heated to boiling and stirred until solution is complete. When cold, the solution is diluted to the same volume as in the other cases.

Yellow Developer: Developer Z (Bayer).—15 parts of developer are dissolved in 20,000 of water.

All the above developing baths are stable, and can be used more than once. Using several developers together in the same bath, in order to obtain fuller tones, is a matter requiring care and experience, because the individual developers do not couple with the same rapidity and completeness, and they are not all suitable for unconditional combination. The best for this purpose are mixtures of β-naphthol with resorcine, and of β-naphthol with diamine.

Sodium carbonate also is occasionally used as a developer; and as a matter of fact it can be employed as such in all cases, though it does not always give such good results as the other agents mentioned. The diazotised material is treated for fifteen minutes, at 40–50° C., with an aqueous solution of 2½–3 % of calcined soda, and then rinsed and dried.

Coupling with the above developers is effected cold or at ordinary temperature. The new azo dyestuff is formed immediately; but to make sure that the whole of the dyestuff is coupled on the fibre, the material is worked about until a constant shade is obtained, which will not take longer than fifteen to twenty minutes at most. The goods are then rinsed, soaped at boiling heat and dried. In the case of toluylenediamine, it is advisable to sour the first washing-water slightly, in order to remove the disagreeable brown tinge.

The dyeings obtained by diazotising are distinguished by their great fastness to washing, and though their fastness to light is only moderate, they are mostly fast to water, and in some cases to over-dyeing as well. Moreover, a number of diazotising dyestuffs that are fast to light are now on the market.

The following dyestuffs, *inter alia*, are suitable for diazotising, β-naphthol or sodium β-naphthol being used as developer unless otherwise specified:—

Red.—Diazo Bordeaux; the diazo brilliant scarlet marks; diazogeranine; diazo light Bordeaux; diazo light red; diazorubine; primuline.

Orange.—Diazo brilliant orange.

Yellow.—Diazo yellow; diazo light yellow.

Green.—Benzo pure blue; brilliant benzo blue 6B; diazo olive.

Blue.—Benzo violet O; diazo blue; diazo dark blue; diazo indigo blue; diazo pure blue; diazo red-blue; diazo black BHN; diazo fast black B and 3B.

Violet.—Diazo light violet.

Brown.—Diazo brown.

Black.—Diazo black; diazo brilliant black; diazo fast black.

(NOTE.—The yellow and green dyestuffs mentioned above are coupled with "yellow developer" or "developer Z" after being diazotised.)

DYEING WITH SULPHONE DYESTUFFS

Chemically considered, the sulphone dyestuffs form a sub-group of the substantive dyestuffs, differing from the other members of that class by the fact that they have a greater affinity for animal fibres (wool in particular) than for cotton. They can therefore be dyed in the same manner as the others, that is to say in a bast-soap bath soured with acetic acid. In general the dyeings on unloaded silk are faster to both light and water than on loaded silk.

The most important dyestuffs of this class, fast to light and water, are sulphone yellow 5G and R, the sulphone-cyanine marks and sulphone-cyanine black. The latter dye silk a handsome full black, that cannot be obtained with acid dyestuffs.

DYEING WITH MORDANT DYESTUFFS

When it is a question of dyeings of the greatest possible fastness to light, air, boiling, soap, water and milling, such as are required for umbrella fabrics, vestments, flags, heavy upholstery fabrics, or for fancy threads, mordant dyestuffs are resorted to. In general, the mordant dyestuffs are antagonistic to the character of silk, as they impair its most important property, lustre. In using these dyestuffs, the silk must be first mordanted, the method of which and the agents used have been already described.

Special care is necessary in the dyeing process, the insolubility or sparing solubility of many of the dyestuffs making the preparation of the bath difficult. The dyestuff, in the form of powder or paste, is stirred up with a ten-fold quantity of water, and the fine sludge is stirred thoroughly into the bath of one-fifth bast soap and four-fifths water, being preferably added in small portions. Owing to the great affinity of the mordanted silk, a better way to prepare the bath is with 1 part of bast soap to 2 of water; 1–2 % of acetic acid is then added, and the mordanted and rinsed, but not dried, silk is entered cold. The acetic acid greatly assists the absorption of the dyestuff, but may, in some cases, lead to parti-coloured dyeings, especially when the amount of dyestuff in the bath is small, in which case the quantity of acetic acid should be reduced or omitted altogether. In fact, the use of this acid is only recommended for dark, full dyeings. The silk is worked constantly in the bath for half an hour, the liquor being gradually warmed to about 90° C. in the following hour, with continued stirring, and kept at that temperature for an hour longer. It is best not to keep the bath on the boil, but only to raise it to that point at intervals, the silk being lifted. Rinsing is followed by two boiling soap baths (3 parts of soap per 1000 of water), a second rinsing, and livening with 10 % of acetic acid in the warm. The silk takes up an extraordinary quantity of alizarine dyestuffs, for instance as much as

20–50 % of alizarine red in paste. Only such mordant dyestuffs as are fast to light should be used.

The mordant dyestuffs are employed to only a restricted extent on silk, the preliminary mordanting and the repeated boiling up of the dye baths having a bad effect on the lustre, feel and elasticity of the fibre.

Matching colours is also a cause of difficulty, the final shade only appearing after soaping. Finally, the usual loading agents cannot be employed. The real purpose of dyeing with mordant dyestuffs is the production of fast colour lakes. According to the general view, the mordanted silk contains a metallic hydroxide fixed in and upon the fibre; and since the alizarine dyestufis have the properties of a weak acid, notwithstanding their insolubility in water, they combine with the metallic hydroxide, in the dyeing process, to form a kind of salt, the colour lake. For example, alizarine-chrome lake is obtained by dyeing with alizarine and a chrome mordant. These metal lakes of the mordant dyestuffs are formed at a temperature approximating to boiling point, and are quite insoluble in water, this property being the cause of the great fastness of the dyeings obtained. In practice, only the chrome, alumina and iron mordants come under consideration for this purpose, and of these the chrome lakes are the fastest in all respects. Alumina mordants are only used for bright and fiery reds and orange shades—though their practical utility is by no means restricted to these alone. Iron mordants are only employed for dark shades.

Red.—The chief mordant reds are alizarine red and alizarine Bordeaux, which are used with both alumina, chrome and iron mordants. Alizarine red gives with alumina mordants a brilliant red; with chrome mordants a dark Bordeaux, and with iron mordants a very dark violet. Alizarine Bordeaux gives with alumina mordants a Bordeaux, with a yellowish or bluish tinge according to the mark used; with chrome mordants an intense violet, and with iron mordants a violet black. In dyeing with alizarine red, water containing lime is preferred, as giving brighter colours; and if the water is soft, a little calcium acetate is added. With alumina mordants these reds will stand boiling, and are fast to water and light, but not to soap or alkalis. On chrome mordants, the alizarine Bordeaux marks are fast to boiling, water, light and alkalis; whereas the alizarine reds are only fast to boiling and light, and neither kind is fast to soap. On iron mordants, both reds are fast to boiling, water, alkalis and light, but not to soap.

Orange.—Alizarine orange R is the only one to be considered. This gives orange with alumina mordants, brown with chrome and blackish-brown with iron mordants. Both the orange and brown shades are fast to everything except soap. The off-colour appearance of dyeings on iron mordants precludes their use.

Yellow.—Chrome mordants alone are used, the dyestuffs including: galloflavine, mordant yellow, anthracene yellow C, diamond flavine, alizarine yellow R and chrome yellow DF and R extra. Of these, diamond flavine and anthracene yellow C will stand boiling, water, alkali and light. Chrome yellow R extra is not fast to washing. Alizarine yellow R and chrome yellow DF are fast to soap, alkali and light.

Green.—For alumina mordants, only cœruleine S and alizarine-viridine FF are used; chromoxane green being employed, in addition to these two, with chrome mordants; whilst cœruleine S alone is used with iron mordants. Cœruleine on alumina is fast to boiling, water, alkali and light; and alizarine viridine, though it will not stand boiling, is fast to soap. On iron mordants, cœruleine is fast to boiling, water, alkali and light.

Blue.—The alizarine blue marks and celestine blue are used on alumina mordants; whilst for chrome mordants, the alizarine blue and alizarine cyanine marks, celestine blue and chromoxane blue R are employed. All are fast to alkali, and all, except celestine blue, to light as well. Alizarine blue and alizarine cyanine are, in addition, fast to boiling, soap and water. Chromoxane blue and celestine blue will stand soap.

Violet.—Alizarine cyanines and galleine are used on alumina mordants; and alizarine Bordeaux B, alizarine heliotrope, chromoxane violet and galleine with chrome mordants. Iron mordants are not employed. In contrast to alizarine blue, alizarine cyanines on alumina mordants give brilliant red-violet shades, fast to everything. Galleine will not stand soap. This latter property apart, alizarine Bordeaux and galleine on chrome mordants are fast to everything. Chromoxane violet is fast to boiling, soap, alkali and light.

Brown.—The anthracene brown marks give, with alumina, chrome and iron mordants, dyeings that are fast to everything but soap. Alizarine orange R also gives a brown (*vide* Orange) with chrome mordants. On these last mordants, chromoxane brown 5R is fast to boiling, alkali and light.

Black.—Alizarine cyanine black G will dye on alumina mordants, and is fast to boiling, water, alkali and light. For chrome mordants, alizarine blue-black B, alizarine cyanine black G and alizarine fast black T are recommended; and the Badische alizarine black will also dye after chrome mordants. For this purpose the makers advise 2 parts of alizarine black in paste to 100 of water, no bast soap or acetic acid being needed. Enter at 30° C., raise gradually to boiling in three-quarters of an hour, boil for an hour and wash thoroughly. The bath, which is not completely exhausted, is regenerated with a further 3–4 parts of the dyestuff paste and used as before. These blacks are of only minor importance in silk-dyeing.

The attempts to simplify the troublesome two-bath method have led to a single-bath method for mordant dyestuffs in silk-dyeing. For alumina mordants, the Badische Co. recommends a bath containing the requisite amount of dyestuff, together with 3 % of alum and 2 % of oxalic acid, the silk being entered at 30° C. and the temperature slowly raised. For chrome mordants, either 3 % of chromium acetate (20° Bé.) and 1½ % of oxalic acid, or 5 % of chrome alum and 3 % of 6° Bé. acetic acid, are recommended. The Farbenfabriken Bayer prescribes adding the properly dissolved dyestuff and 2–5 % of formic acid to the bath at 40° C., entering the material, heating slowly to boiling and working for one hour at that temperature. If the bath does not draw sufficiently, a further addition of formic acid is given. The goods are finally treated, in the same or a fresh bath, with chromate of potash, for a half to three-quarters of an hour.

It should be mentioned that the single-bath method is not applicable to all mordant dyestuffs; in fact, only a comparative few of them are suitable, such as the following, recommended by the Farbenfabriken Bayer: alizarine red W, anthracene yellow C, chrome yellow D and R extra, diamond flavine G, alizarine cyanine RR, chromoxane blue R, chromoxane violet B, 5B and R, alizarine orange R, chromoxane brown 5R, diamond black F, P2B, PV and PVB.

Since, whenever silk is dyed with mordant dyestuffs, a colour lake insoluble in water is formed on the fibre, the silk also becomes loaded at the same time. The loading is, however, unintentional, inconsiderable and—what is particularly important—entirely harmless.

Dyeing with Sulphur Dyestuffs

It should be premised that the author is not at all enamoured with the use of sulphur dyestuffs for silk, since he considers the process unnatural and quite superfluous. Silk can be dyed all imaginable shades of colour and degrees of fastness with basic, acid, faintly acid, substantive, diazotising, sulphone and mordant dyestuffs, so that there is no reason for employing the sulphur dyestuffs, the method of dyeing which endangers the stability of the material. It is well known that, in order to dye with sulphur dyestuffs at all, they must be dissolved in up to four times their own weight of sodium sulphide. Moreover, since most sulphur dyestuffs are not chemically pure products, but crude melts, of which frequently from 10–25 % of the weight of the goods under treatment must be used, it may easily happen that the weight of sodium sulphide exceeds that of the silk itself. Now, sodium sulphide is a powerful alkali, and strong alkalis act injuriously on the silk fibre. This fact is known, and for a long time retarded the application of the sulphur dyestuffs in silk dyeing. Meanwhile, attempts have been made to find some agent capable of counteracting the injurious influence of sodium sulphide, additions of gelatine, tannin, lactic acid and sodium lactate having been suggested. It is admitted that such agents ameliorate the action of sodium sulphide, but they by no means neutralise it altogether. The author is not an opponent of sulphur dyestuffs. He freely and fully recognises their valuable properties, and likes to use them for dyeing cotton and artificial silks—but not for silk. Both he and his pupils have tried dyeing silk by all the different methods proposed for the sulphur dyestuffs in association with sodium sulphide, but invariably without success. In no case did the silk come out of the dye-bath uninjured, and he, personally, would therefore never employ these dyestuffs for silk. If, nevertheless, other dyers consider themselves more courageous or possessed of greater skill, they may try at their own risk. It may be freely admitted that a method which would secure complete immunity of the silk fibre would constitute an important improvement in the silk dyeing industry, since most of the dyeings in question are proof against light, ammonia, water, washing, boiling and over-dyeing.

The following recipe is given by the Farbenfabriken Bayer :—

Dyeing with Katigene Dyestuffs.—The katigene dyestuffs, crystallised with sodium sulphide, are dissolved as usual, and the solution is introduced into the dye-bath, 20–40 % of common salt being added, followed by 1½ parts (based on the weight of sodium sulphide) of sodium acid lactate, added by degrees and well stirred in. In dyeing with katigene black T3B, which gives the handsomest black on silk, the amount of sodium lactate should be 2–2½ times the weight of the sodium sulphide, and preferably also a little Turkey-red oil or monopol soap, together with about 7 oz. of gelatine per 100 galls. of bath liquor. The sodium lactate neutralises the injurious action of the sodium sulphide and causes the bath to draw more completely.

Colours are preferably dyed at 50–60° C., and blacks at 80–90° C., the material being mounted on iron rods and kept submerged in the bath for an hour.

Another method consists in dyeing the katigene dyestuffs with caustic soda and hydrosulphite in a 1:40 bath, the following recipes being typical :—

Coloured Kaligene Dyeings.—For a 15 % dyeing, 3–5 c.c. of 30° Bé. caustic soda, 1½–2½ grms. of hydrosulphite (conc. BASF powder) and 30–40 grms. of common salt, per litre of bath liquor, are used.

Katigene Black.—For a 40 % dyeing, 13–15 c.c. of caustic soda, 5–6 grms. of hydrosulphite and 50 grms. of common salt are added per litre of bath liquor. The dyestuff is made into a paste with caustic soda and warm water (about 60° C.), the hydrosulphite being then strewn in, and the mixture left until the dyestuff has dissolved. The salt is dissolved in the bath liquor, and the dyestuff solution added afterwards. The goods, preferably submerged, are dyed for an hour at 60° C., rinsed, hung for a short time, soured with acetic or formic acid, rinsed, soaped boiling hot, again rinsed, and brightened with acetic or formic acid. This second method has been in use for some time for the hydrone dyestuffs (Cassella), which may be regarded as intermediate between the sulphur and vat dyestuffs.

Dyeing with Vat Dyestuffs

The vat dyestuffs, of which indigo was the sole representative for centuries, have largely increased in number of late years, and have attained a very high degree of importance. The pioneer was the Badische indanthrene, an extremely handsome, clear blue vat dyestuff, and this was soon followed by others of the same group, such as flavanthrene, violanthrene, etc. At about the same time the various halogen derivatives of artificial indigo made their appearance on the market, all of them fast blue vat dyestuffs. Then followed the algol dyestuffs (Farbenfabriken Bayer), ciba and cibanone dyestuffs (Soc. Ind. Chim. Basle), and the helindone dyestuffs (Farbwerke Höchst). At present, the entire gamut of colours can be dyed with vat dyestuffs. Indigo, the "king of dyestuffs," which was formerly enthroned on an isolated elevation, has now many powerful competitors, and is no longer regarded with the devotional awe of former days, being at present barely *primus inter pares.*

All these new dyestuffs can be dyed in the vat like indigo; that is to say, the insoluble dyestuffs are converted into the soluble condition, or "vatted," by treatment with reducing agents in the presence of strong alkalis. The resulting solution constitutes the vat, and in this the silk is dyed, with or without heat. The fermentation vat, which is the one most extensively used for wool, is not employed for the new dyestuffs; neither is the vitriol vat, used for cotton. For the indanthrene and algol dyestuffs, the hydrosulphite, or more rarely the zinc dust and bisulphite, vat is employed.

These new dyestuffs, which at first were only used on cotton, have recently been extended to dyeing silk, on which they give remarkably fast colours. The prime materials from which they are produced are, however, expensive, which accounts for the limited use of these dyestuffs in spite of their incomparable fastness. But, whilst they are too dear for cottons, such a costly material as silk can very well bear the extra outlay involved.

It is impossible to do more than give a general outline of a method of dyeing that is applicable to all the vat dyestuffs. These materials are almost always sold in paste form; but directly the pastes are stirred up with water, differences make their appearance. The makers recommend that the water for stirring should either be cold, at 25–30° C. or 40–50° C., according to the dyestuff used. The next step is to stir in the total quantities of caustic soda (30° Bé. strength) and hydrosulphite (concentrated powder) required for the bath, the mixture being allowed to stand until reduction is complete and the solution has clarified. Generally, the colour of this solution differs considerably from that of the resulting dyeing. This solution is the " vat " of the corresponding dyestuff, that is to say, the leuco compound of the latter; and it exhibits most of the properties of the well-known yellow indigo vat. This latter forms on the surface a delicate film, with a coppery sheen, resulting from the oxidation to indigo of the calcium compound of indigo white at the surface. Similar oxidation phenomena are produced on all the vats of the new vat dyestuffs, which, however, are not always yellow, but of various colours, the vat from algol yellow R, for example, being dark reddish-brown, whilst that from algol red is dark violet. Nevertheless, the aforesaid film, the " bloom," or scum on the surface, is always the same colour as the final dyeing.

To set the dye bath, the beck is filled with the requisite amount of water, to which is added, prior to the dyestuff solution, 1½–2½ c.c. of 30° Bé. caustic soda and 1¼ grm. of concentrated hydrosulphite powder, to every 10 litres of bath liquor. This is followed by dissolving the necessary quantity of Glauber salt, which varies with the dyestuff, being omitted altogether in some cases, whilst for others as much as 400 grms. per litre are required. As soon as this salt is dissolved, the dyestuff solution is added, and the bath is ready for dyeing.

Each vat dyestuff must be used at the particular temperature that is most suitable; and according as this characteristic temperature is low or high, the dyestuffs may be classified into cold- and hot-dying respectively. Accordingly, the bath temperature for the former is at ordinary temperature or about 25–30° C., whilst for the others it is 60° C. In order to ensure complete and uniform penetration of the material by the dyestuff, and at the same time prevent partial local oxidation by the oxygen of the atmosphere, it is best to keep the goods submerged for three-quarters to one hour. They are then reeled out, without rinsing, and "hung" for a half to three-quarters of an hour, to oxidise, or "green," being afterwards rinsed and soured in the cold with 1–2 parts of commercial sulphuric acid per 1000 of bath liquor. It should be mentioned that although the colour changes during the hanging stage, the final shade only appears in the souring bath. Acetic or formic acid may be used instead of sulphuric acid for souring. Finally, the dyed material is again thoroughly rinsed, and soaped in the warm, or preferably at boiling heat. This method may appear too complicated to some readers, and as a matter of fact it is so; but it should be remembered that dyeing indigo by the vat method is just as troublesome. The goods have to be entered in quite as many baths, vatted, dyed, soured and rinsed; and there is in fact no difference. The whole matter, however, looks much worse on paper than it is in reality, the process being far simpler than indigo dyeing, which takes hours, sometimes days, to prepare the vat, whereas in the present case the vat is ready for dyeing in half an hour, and the whole process, soaping included, is over in two hours. Moreover, these new dyestuffs give a degree of fastness previously unattainable, and in addition to the ordinary kinds of fastness already mentioned, many—not all—have the extra advantage of being fast towards chlorine, and will stand scouring with raw silk and cotton, and the subsequent bleaching with hydrogen peroxide.

The foregoing is a general outline of the dyeing process; but there are so many modifications and exceptions in the case of the individual dyestuffs that it is impossible to go into all the details here. Even the point whether the operation must be performed cold or hot would necessitate the enumeration of the whole series. Those who wish to adopt the new method should consult the makers of the dyestuffs as to their special peculiarities, and also as to the requisite quantities of alkali, hydrosulphite and Glauber salt to use.

A number of the vat dyestuffs distribute with difficulty, and it is particularly difficult to get uniform dyeings with mixtures—a problem which has not yet been satisfactorily solved.

To obtain rapid and uniform oxidation of the dyestuff, the material—piece goods especially—should be entered, directly after squeezing, in a long bath, at hand temperature, containing 1½–2% of chromate of potash and 3–4% of acetic acid, based on the weight of the silk, the goods being treated for about a quarter of an hour, then rinsed thoroughly and soaped. This after-chroming is particularly adapted for combination dyeings with the aid of the jigger, into which (charged with the above ingredients) the goods are entered after squeezing.

The zinc dust and bisulphite vat recommended by the Badische Co. for pure indigo BASF is prepared as a stock vat from 10 kilos. of the dyestuff paste and 30 litres of 20% milk of lime (= 3 kilos. of CaO), together with 10 litres of 32° Bé. bisulphite into which 1 kilo. of zinc dust has been slowly stirred. This last-named mixture is left to stand for about a quarter of an hour, with careful stirring, until the mass has become hot and turned pale green, whereupon it is mixed with the indigo and lime, and made up to about 90 litres with water at 28° C. When completely reduced, this stock vat is added to 1000 litres of bath liquor, and at the end of a few hours will be ready for use. As soon as the liquor assumes a greenish shade it is quickened with 1–2 litres of 32° Bé. bisulphite mixed with 100–200 grms. of zinc dust, followed, after a quarter of an hour, by $\frac{1}{4}$–1 litre of 20 % milk of lime, together with a further quantity of stock vat as required. This vat will give full, handsome shades.

DYEING WITH NATURAL DYESTUFFS

The consumption of natural dyestuffs for dyeing silk is very small in comparison with what it used to be, colours being now dyed exclusively with artificial organic dyestuffs. On the other hand, logwood is still extensively used for black, notwithstanding the large number of artificial black dyestuffs available and the far inferior fastness of logwood dyeings. This remarkable contradiction is based on two reasons : in the first place, logwood is much cheaper, and in the second it loads the silk, which the artificial blacks do not do. It may be averred that most black on silk is dyed with logwood, by methods which will be described later.

Natural indigo has been completely displaced by the artificial product, the application of which has already been described.

Fustic and fustic extract are no longer used for yellow, but only for shading logwood black, especially when it is desired to suppress the blue sheen of logwood black and produce a full deep black. For this purpose, fustic is generally boiled along with the logwood, the extract, on the other hand, being added to the logwood extract.

Of the other natural dyes, orchil is the one most largely employed. It gives bright dyeings scarcely inferior to those from artificial dyestuffs, and it equalises well, whilst the dyeings are just as fast as the same shades obtained with acid dyestuffs. Orchil can be dyed with soap, and also with bast soap, with or without addition of acetic or sulphuric acid.

Cochineal is still occasionally used by the older dyers, but has been displaced by such acid dyestuffs as cochineal red, cochineal scarlet, coccine, azococcine, azocochineal, etc., owing to the simpler method required.

Weld, and more rarely weld extract, still plays an important part in silk-dyeing, on account of its fastness to light and, to some extent, to soap as well. It is dyed on alumina mordants, which, however, must be perfectly free from iron if a pure yellow is desired. The decoction (from 20–40 % weld) is prepared with carbonate of potash, and a little Marseilles soap is added, the amount depending on the hardness of the water. After dyeing, the colour is livened, without previous rinsing, with a little woad decoction or acetic acid. If necessary, the yellow is shaded with a little Orleans. Chrysophenine has recently been employed as a weld substitute for a strong yellow with reddish tinge, and chloramine yellow GG for paler shades. This latter has the advantage of being fast to acids, which the other two are not.

Tumeric, strangely enough, is still used for dyeing silk, although the resulting shades are fugitive to light and sensitive to alkali. The silk is dyed, either direct in the aqueous extract from the root, or with addition of a little acetic acid or alum; soap should not be used. The dyestuff, however, is never employed alone, but always in combination with others, such as fuchsine and logwood, for English brown; or cutch and logwood, for Russian green.

Indigocarmine has almost gone out of use, on account of its very poor fastness to light. Quercitron is occasionally employed, like fustic, for darkening logwood. The other natural dyestuffs have disappeared from silk-dyeing practice.

BLACK-DYEING SILK

Of all shades, black is the most extensively produced on silk, and it may be asserted that more silk is dyed black than all the other colours together. For this reason, the black-dyeing and colour-dyeing of silk form two separate industries, there being many large works which dye blacks exclusively, and are therefore able to turn out a specially fine article. It is therefore necessary to go into the subject of black-dyeing more closely, although, in the entire absence of any scientific methods, it is not a pleasant one for a teacher who desires to instruct his students. Whilst it can be confidently stated that dyeing at the present day is established on scientific foundations, this does not apply to the black-dyeing of silk, the old empiricism still prevailing with undiminished intensity; and it is almost impossible to convert this chaos into order. Moreover, loading is closely connected with black dyeing, the two operations being often so intimately intermingled that it is impossible to separate them.

The two chief materials for black-dyeing are logwood and iron gallotannate (the colouring matter of black ink). The methods of using each are innumerable, and, finally, the two are nearly always employed in combination. This explains the great number of dyeing recipes which, although differing widely in detail, all lead more or less to the same result, viz. a logwood black dyed on an iron ground or topping an iron gallotannate black. The reason for the great variety of recipes employed in practice resides in the multiplicity of the materials from which logwood black can be prepared, and also in the divergence of the iron mordants and the tannins used for the iron gallotannate black. Every black-dyer works according to his own formulæ—which are usually kept secret—and believes them to be the best and most reliable. Out of the mass of recipes which have thus come into existence, there is not one that is really simple, most of them being so complicated that the vat-dyeing process is merely play by comparison. It is really marvellous to see what has been dragged into these formulæ, and still more astonishing when one tries to ascertain the why and wherefore of it all! It must be remembered that black silk without any loading is rarely, if ever, met with in commerce; and although the art of the dyer has attained its greatest triumphs in the black-dyeing of silk, no one can say whether the dyeing or the loading is the actual object of the treatment. Unfortunately, it must also be admitted that the methods of dyeing are admired and esteemed in proportion to the number of operations employed, although not the slightest explanation can be given for many of these quite purposeless manipulations.

It is impossible here to go into the value, or otherwise, of these innumerable recipes, for a whole book could easily be written on the subject, and the author will therefore content himself with endeavouring to set out the scientific basis of the rational production of logwood and iron blacks.

Black-dyeing with Logwood.—The general rule in practice is to employ logwood decoctions, the use of extracts being avoided because of the uncertainty as to whether they have not been adulterated with chestnut extract, and the like. Of course, not the slightest objection could be urged against the use of pure logwood extracts for dyeing silk. But, as a matter of fact, the commercial extracts are never employed for high-class goods, though they are admissible for ordinary deep black or brownish black.

Although the colouring matter of logwood is highly sensitive to copper, the logwood chips can be boiled in a copper pan, inasmuch as, at the first boiling, that portion of the metal which is in contact with the liquor becomes coated with a black film which protects it from further direct contact with the liquor and prevents any further action of the copper on the colouring matter. When perfectly soft water has been used, the resulting decoction is yellow to brownish-yellow, whilst that from hard water is reddish-violet; and the yellow solution at once turns to red-violet on addition of lime, soda or ammonia. In working with these liquors, especially when reddish-violet, they must be kept, as far as possible, from contact with the air; otherwise the colouring matter is liable to decompose quickly, turning a dull brown in one to two hours and no longer suitable for dyeing. As the logwood baths never become completely exhausted of the dyestuff, they are kept. Moreover, old baths have generally greater tinctorial power than when fresh, because a portion of the contained hematoxylin is already oxidised to hematin.

Black-dyeing with logwood is mainly an oxidation process, the colouring matter, hematoxylin, being oxidised into hematin by the action of the iron salt of the mordant used; whilst at the same time the hematin, in the nascent state, combines with the iron of the mordant to form an insoluble blue-black compound. The resulting hematin-iron lake is the actual cause of the blue-black appearance of the dyed silk, but it does not increase the weight of the fabric. The method of dyeing is as follows:

1. Enter for two hours in cold basic ferric sulphate (15° Bé.).
2. Rinse, first cold, then warm.
3. Dye in a decoction of 125% of logwood, in presence

of 20 % of Marseilles soap, entering at 20° C., gradually warming up to near boiling, and keeping at a gentle boil for one and a half hours.

4. Drain in the hydro-extractor and dry. If necessary, brighten with an emulsion of olive oil and soda before drying.

Silk dyed in this manner is used as weft for gloves.

Möhlau recommended the following method for a light black on silk: Mordant in a cold bath (density 25°Bé.) containing equal parts of basic iron sulphate and iron pyrolignite, and dye at 70° C. in a logwood decoction shaded coal-black with fustic, followed by immersion in a bath of logwood and soap, finally brightening with oil.

Hummel mentions the two following recipes for dyeing silk black without loading :—

Black for Hat Plush.—Mordant in cold basic iron sulphate, and wash. Dye in a logwood decoction with a little fustic extract, 1–2 % of copper acetate and 5–10 % of ferrous sulphate being usually added. Dye in a decoction of logwood and soap, and brighten with oil.

English Black.—Mordant with basic ferric sulphate for two hours, followed by washing and soaping at 85–90° C. Dye with 50 % of fustic, 10 % of ferrous sulphate and 2 % of copper acetate. Dye with logwood and soap, and brighten.

The Rapid Black method, so called because it only takes 3–4 hours, also belongs to the non-loading class. The silk is entered and continuously worked for two hours in a bath containing a decoction of 20 % of fustic, 5 % of Gambier cutch, 4 % of copper sulphate and 20 % of ferrous sulphate; then rinsed, drained in the hydro-extractor, and finished in a bath containing 200 % of logwood and 25 % of soap.

The same category also includes the comparatively rare operation of dyeing raw silk black, in which a certain amount of care is required to dye the silk without removing the bast. On this account the number of operations must be kept as small as possible, and the dyeing conducted at low temperatures. The silk is first treated in 1–2 iron baths, and then dyed with logwood and fustic—but without soap—at 50–60° C.

For light logwood blacks the mordanting with basic iron sulphate is sometimes omitted, being replaced by a browning process in which the silk is treated for about an hour with 50% of logwood, 30–50% of fustic, 5–6% of ferrous sulphate and 2–3% of copper acetate, entering at 50° C., working for half an hour at 60° and for a similar period at 70°, then exposing to the air for three-quarters to one hour and washing repeatedly. Finally, the material is dyed with logwood and soap. The shade produced by the preliminary treatment is to some extent a half-finished single-bath logwood black, which serves as a bottoming, and also as a mordant, for the subsequent dyeing. The exposure to the air produces an oxidation which fixes the colour lake.

As a rule, however, the black-dyeing of silk with logwood in practice is a far more complicated process, because it is accompanied by loading.

The foundation of all blacks on silk consists of compounds of tannic acids and iron, with or without the assistance of other dyestuffs, such as logwood, Berlin blue or the like. The logwood acts by virtue of its hematoxylin and tannin. Tanning agents (cutch, gallnuts, divi-divi, etc.), are employed for choice, because they give a deeper and brighter colour.

Dyeing and Loading with Tannins and Iron Salts.—It is well known that gallnut decoction, or commercial tannin, gives a grey to black with ferrous sulphate solution, the simplest form of the product being ordinary black writing ink. Exactly the same black can also be produced, from the same ingredients, on the silk fibre. It has already been mentioned that silk can be loaded with tannin agents, and that this loading is only valuable when the tannin is fixed with iron, the formation of iron gallotannate producing a blue-grey to blue-black according to the quantity of materials taken. For darker shades, the goods are returned from the iron bath to the tannin bath, and then to the iron bath once more, these manipulations being repeated as often as necessary. Of course, each additional absorption of tannin and iron increases the degree of loading, *pari passu* with the depth of colour. This method is known as bottoming, the substances deposited in the silk fibre constituting the foundation for the subsequent dyeing or for further bottoming. Iron tannate produced on the fibre by the above treatment forms "iron bottoming," that is to say, a loading with iron gallotannate; and the bottoming is single, double or treble, etc., according to the number of times the treatment is repeated. A different type of iron bottoming can be obtained, according as basic iron sulphate or iron pyrolignite is used, the former being a ferric, and the latter a ferrous salt which has to be converted into the ferrous state on the fibre. The use of sumach, gallnuts, divi-divi, etc., in place of tannin, has already been referred to. Every black produced in this way is a pure gall black.

The tanning agents furnishing gall blacks give a blue-black precipitate with iron, and are known as iron-bluing tannins, to distinguish them from those forming a greenish-black precipitate. The most important of them is catechu, or cutch, both commercial qualities of which—Pegu and

Gambier—are largely used in silk-dyeing. Cutch contains two valuable constituents: catechin, which plays an important part in dyeing cotton brown, and catechutannic acid, which forms a green compound with iron and is of special import in the dyeing, or loading, of silk, because the fibre takes up and fixes, so as to be waterproof, 40% and more of this substance even at 40–50° C. On the other hand, the bluing tannin constituent of sumach and gallnuts is only absorbed at higher temperatures and in smaller quantities. Moreover, the silk swells up far more on absorbing the cutch tannin than it does when treated with sumach tannin—all of which properties favour the use of cutch for loading purposes. Any coloration of the silk by the catechin is relatively negligible.

On the other hand, cutch has the disadvantage that the iron compound of catechutannic acid is of an ugly green colour, which is not easily masked by other colour lakes, whereas sumach tannin gives agreeable blue-black, which may even be used as a self colour. As a matter of fact, gallnut black is a shade produced by the repeated treatment of silk with a decoction of gallnuts and an iron mordant; but no similar shade can be obtained from cutch alone. This is the reason why cutch is preferred for heavy loadings, and for its employment in combination with logwood.

The iron bottoming is produced by entering the silk in a solution of basic ferric sulphate (30° Bé. strength), a yellow coloration being obtained. The treatment may be repeated several times. On now fixing the iron with cutch, the ugly, blackish-green iron catechutannate is formed.

Such a loading with iron is termed cutch bottoming. The usual method adopted in practice is, however, different.

At first, the silk is bottomed one or more times with iron, and this is transformed into Berlin blue, forming a blue bottoming, the operation being termed bluing. Not until this stage is completed is the material subjected to the action of the tanning agents, sumach or gallnut extract.

The bluing is effected by treating the iron bottoming with ferrocyanide of potash and a little hydrochloric acid, the object of this treatment being, on the one hand, to prevent the iron mordant from oxidising the tannin and reducing the ferric salt at the expense of the latter; and on the other to produce insoluble Berlin blue, which has a favourable influence on the unpleasant green shade of the subsequently produced iron catechutannate, at the moment of formation. Such a Berlin blue bottoming will absorb tannin below 50° C. without any mutual reaction being observable, such action only taking place above that temperature. The nature of this reaction has not yet been definitely established, but presumably it consists in a partial reduction of the iron salt at the expense of the tannin, so that the compound on the fibre probably consists chiefly of ferro-ferric catechutannate together with undecomposed Berlin blue and japonic acid in variable proportions. This forms the cutch bottoming. The usual method of preparing it in practice is by entering the deep-blue coloured silk for an hour, or over-night, in a bath containing 100–200% of cutch, at 60–70° C. The loading can, of course, be still further increased by additional alternating treatment with basic ferric sulphate, ferrocyanide and cutch. Numerous modifications are practised, one of them, for instance, being to omit the bluing of the (single to treble) iron bottoming, and replace this by boiling with soap, finishing up by treatment with 100–200% of cutch in a boiling bath.

The silk bottomed by one or other of the above methods is therefore not merely loaded, but also mordanted, with iron, and dyed the shade peculiar to the iron bottoming; and, as a result of the iron mordanting, it is, of course, enabled to fix any of the mordant dyestuffs in the form of iron lakes. This property, however, is not utilised in practice, because, in consequence of the dark colour of the iron bottoming, only dark shades approximating to black—such as blackish-brown, blackish-green, blue-black, or the like—can be obtained; and these dyeings, although fast, can be produced in cheaper ways. As a matter of fact, silk bottomed with iron is almost invariably dyed black with logwood, with or without fustic (or with logwood and fustic extracts). Unfortunately, loading and dyeing are completely amalgamated, although there is no inherent connection between them, for it is quite possible to dye silk black without loading, and also to load it properly without dyeing it black. In the black-dyeing industry, loading and dyeing are inseparable, which explains why logwood-chrome black is never produced, for, though it is easy to dye, and is both handsome and fast, it does not add to the weight.

According to the degree of loading to be produced, blacks are classified into light, medium and heavy, the latter being, of course, the most popular though, in reality, the least valuable, because it must be evident to any intelligent person that a heavy black contains only 50 %, or even less, of silk, so that the material has no longer any real claim to be considered silk at all.

The true purpose of the present defective system of black-dyeing is therefore to incorporate the silk fibre with as much ferric gallotannate, catechutannate and moringatannate as possible, together with iron cyanocyanide, in addition to the compounds of iron with hematin and morin, the two black colour lakes. The various ways in which this purpose is achieved in practice have been set out above, and afford an explanation of the great multiplicity of recipes for black-dyeing silk. The variety is due to the differences in the repetition of the various processes, changes in their serial order, modifications in the working conditions and the duration of the several stages, the employment of higher or lower temperatures, etc.

The following recipes are selected from the author's extensive collection, compiled from the technical literature.

Chestnut Black.—This gallotannate black, which is the kind most extensively produced in Germany, is prepared with chestnut extract in place of gallnut extract, the raw silk being treated alternately in baths of iron pyrolignite and chestnut extract, the temperature of the first bath being raised to a degree suitable for softening the silk. According to the degree of loading desired, 10–15 baths are given, the weight being increased 300–400 %. Instead of brightening, olive oil is used in the final treatment. Owing to the impurities contained in the chestnut, the black is mostly dull, but the brightness and colour are improved by bottoming with Berlin blue, or by topping with logwood, at 50–60° C., without soap.

Lyons Black.—The silk is mordanted in cold basic ferric sulphate solution (30° Bé.), rinsed, entered in a soap bath at 85° C., and dyed in a separate bath with 15–20 % of ferrocyanide and hydrochloric acid. When the (Berlin blue) colour is developed, the silk is returned to the first iron bath, rinsed, and then dyed in a bath of 50–100 % of cutch at 50–60° C. The silk is next topped with logwood, by entering it in a cold alum mordant, washing on the machine, and dyeing in a fresh bath with a decoction of 20 % of logwood and 5 % of fustic, in presence of a little soap. The final treatment consists in brightening with oil. This black loads the silk about 10 %.

Mineral Black is less handsome than the foregoing, and is chiefly used for silk linings. It is obtained by mordanting with basic ferric acetate, followed by washing, bluing with yellow prussiate and hydrochloric acid, mordanting again with the same iron bath, fixing with 100 % of cutch at 80° C., dyeing with logwood and soap, and brightening. The increase in weight is 35–40 % or more.

Velvet Black.—The silk is first bottomed with alkali blue, then mordanted and soaped in the same way as for Lyons black, and dyed in a fresh bath with 40 % of fustic, 8 % of ferrous sulphate and 2 % of copper acetate. The next stage is topping with logwood and a little soap, followed by oiling. In this method the degree of loading obtained is hardly worth mentioning.

Souple Black (Gillet & Sohn).—The silk is mordanted with basic ferric sulphate as already described, entered in a soda bath, blue with yellow prussiate, and softened by treatment, at 70–75° C., for one to three hours according to the quality of the silk, in a bath consisting of a decoction of gallnuts, divi-divi, etc. On cooling, 5–10 % of stannous chloride are added, and finally the silk is soaped with 60–80 % of soap at 25–30° C. and brightened with 10–15 % of olive oil. The extent of the loading depends on the number of iron baths, one bath giving an increase of 40–60 %; two, 60–70 %; three, 80 %; and four, 80–100 %.

Heavy Black.—This is more particularly applied to atlas twills, taffetas, etc. Mordanting and soaping are conducted as for Lyons black, the treatments being repeated alternately up to ten times, after which the silk is blued, with prussiate and hydrochloric acid, also in the same way as for Lyons black. Next follows a bath of

100–150 % of cutch, in which the silk is worked for some time at 50–65° C., with addition of 10–15 % of tin salt, this bath being succeeded by a second, of higher concentration. The dyed silk is topped with logwood black, by mordanting it with iron pyrolignite, dyeing in a fresh bath of logwood and soap, as already described, and finally brightening in an oil bath.

Loaded Cutch Black.—The silk is treated in a bath of basic ferric sulphate (28° Bé.), the iron being fixed in a hot bath with 65 % of soap, the treatment being repeated in accordance with the degree of loading required. It is then blued with prussiate and hydrochloric acid, treated in a bath containing 200 % of cutch and 6 % of tin salt, and dyed with 600 % of logwood and 60 % of soap. After entering in a bath of iron pyrolignite, the silk is returned to the old cutch bath, re-dyed with logwood and soap, and finally brightened with acetic acid.

Medium-weight Cutch Black (Silbermann).—The first four stages are the same as for Mineral Black, the silk being then well washed, and treated in a bath of iron pyrolignite (2–3° Bé.) at 25–30° C. At the end of half an hour it is exposed to the air, well washed, and entered in a cutch bath (4–5° Bé.), in which it is worked for half an hour at 40–50° C., being finally dyed with 100 % of logwood and 40–50 % of soap at 50–60° C. (not higher).

It is a deep, full black, with bluish tinge, which must be taken out of the dye bath quickly and repeatedly well soaped. The loading is 40–50 % and over.

Heavy Black with Cutch and Tin Salt.—The raw silk is treated for two to two and a half hours in a bath of pink salt (30° Bé.), the tin being fixed with a boiling-hot bath of 20 % of ammonia soda and 4 % of soap. These operations must be repeated in accordance with the amount of loading required. A single treatment with pink salt increases the weight by 40–50 %; two, by 50–90 %; three, by 90–120 %; and four by 120–150 %. The tin-loaded silk is packed in bags and scoured for one and a half to two and a half hours with 30 % of soap and 5 % of carbonate of potash. The next stage is mordanting with basic ferric sulphate (30° Bé.), 3–8 times, which gives an increase in weight (referred to the raw silk) of 30–150 %, or, including the tin loading, 70–300 % in all. After each iron bath comes a boiling-hot fixing bath of ammonia soda and soap, followed by a light rinsing. The silk is then blued with prussiate and hydrochloric acid, and treated with 150–500 % of cutch, according to the loading desired, the best plan being to work the silk about several times and leave it immersed all night, at 70° C., 8–13 % of tin salt being mostly added, which lightens the colour of the bath—presumably by reduction. Next morning, the silk is carefully washed, and then treated for a half to one hour in a bath containing 30–50 % of soap, at about 50–60° C. This is followed by entering in an old cutch bath (without tin), replenished with 70–310 % of cutch according to requirements, and washing is succeeded by dyeing with logwood. Owing to the large amount of tin on the fibre, the blue has a strong reddish tinge, and on this account it is a frequent practice to interpolate a bath of iron pyrolignite before dyeing with logwood, following it up with a third cutch bath in order to obtain a black which is comparatively fast to rubbing. The dye bath is charged with 100–200 % of logwood and 50–60 % of soap, the working temperature being 50–75° C. By this means the silk can be loaded to the extent of 600 % or more.

This method can, of course, be correspondingly modified by resorting to the tin-phosphate method of loading. In such case, the tin from the pink salt baths is fixed with sodium phosphate, instead of ammonia soda and soap, and the subsequent iron baths are fixed in the same way. All the other operations remain unchanged.

New Blue-Black (Steinbeck).—Organzine is bottomed in three iron baths (30° Bé.); blued with 20% of prussiate and 32% of hydrochloric acid; treated with 130% of cutch (without tin), being entered at 75° C. and left immersed over-night; treated for one hour with iron pyrolignite (4° Bé.); hung for half a day and well washed; rinsed in a light cutch bath; dyed with 200% of logwood and 60% of soap and brightened with lemon juice or olive oil.

These recipes should suffice. It would be easy to give double the number, there being any quantity to chose from, but no new facts would be brought forward by doing so. The variations are comparatively slight and mostly relate to the basic ferric sulphate treatment, and more rarely to the pyrolignite, Berlin blue, the choice of the tanning agent, or to the pink salt, sodium phosphate or logwood.

The difficulties of the black-dyeing process are further intensified when one has to deal with fancy yarns, that is to say, with goods composed, not of reeled silk threads, but of threads twisted from broken filaments. These materials being unable to stand so many treatments, the whole method has to be simplified, in order that the fibres may retain their smoothness and lustre. Consequently, heavy loading is renounced, more particularly as the goods are made of cheap waste fibres.

English Black on Chappe Silk (Silbermann).—The silk is bottomed, cold to hot, in a bath of fustic extract, ferrous sulphate and copper sulphate, being then washed and dyed in a logwood bath. This is a rational black, being capable of scientific explanation, simple in dyeing and furnishing a very popular fast black, without any loading. Of course, when loading is desired, the silk must be bottomed with iron, fixed with hot soap, loaded with cutch and dyed with logwood and fustic. These complicated methods, however, more or less impair the quality of the fibre. Loaded blacks on chappe, floconnet, cordonnet and similar goods correspond to the same blacks on pure silk, but stronger baths and higher temperatures are used. Loadings up to 30–60 % are obtained by a single bottoming with iron, bluing, and treating with cutch, with or without tin salt, etc., and heavier loadings by the gallnut black method (with or without bluing), using gallnut extract for finer shades and chestnut extract for ordinary.

All attempts to replace logwood, wholly or in part, by artificial organic dyestuffs have failed, so far, to give satisfactory results. The black acid dyestuffs, which would seem to be the most appropriate, have not sufficient tinctorial power on silk, 10–15 %, and even more, of the dyestuff being required, and even then, merely a dark blue-black, violet-black or blackish-green is obtained, that is not to be compared with logwood black, although the dyeings are superior in point of fastness to light and acids. Moreover, they give no increase in weight, and finally cannot compete in respect of cost. The black diazo dyestuffs, too, have made but little headway; and it has already been pointed out that there is little prospect for the mordant dyestuffs to compete with logwood, which itself belongs to that category.

Finally, mention may be made of Aniline Black, which seems a likely competitor of logwood in respect of cost. Attempts to produce aniline black dyeings on silk date as far back as 1867; but little progress has been made in the interim, for even now the dyeings cannot be regarded as satisfactory, it being very difficult to get uniform distribution. The most important methods are those of Gonin and Glanzmann, Lauth and Steinbeck, which are briefly outlined below.

Gonin & Glanzmann (Fr. Pat. 82552) use a mixture of 100 parts of chlorate of potash, 100 of sal ammoniac, 250 of aniline salt and 125 of aniline nitrate, the silk being impregnated with a solution of these salts, and the black developed by oxidation, preferably by moist heat.

Lauth (Fr. Pat. 82554) proceeds in a similar manner, but employs as oxidising agent, in place of aniline nitrate, the manganates or permanganates of barium or copper, or lead peroxide. He first fixes these highly oxidised, insoluble substances on the fibre, and then dyes in a bath containing 50 parts of aniline and 100 of hydrochloric acid per 1000 of water.

Steinbeck prepares a bath containing 10–12 % of aniline oxalate and 8–10 % of cupric chromate, 5 % of sodium chlorate being dissolved separately and added to the cold bath. When the silk is entered, the bath temperature is gradually raised, while the material is being worked about, so as to attain 65–70° C. in about two hours. The silk is thereupon treated for half an hour with 2 % of bichromate of potash, and is soaped, boiling hot, for an hour, being finally brightened with acetic acid and oil.

According to an English recipe, published a long time back in the *Dyer and Calico Printer*, 5 parts of aniline oil and 7½ of hydrochloric acid (22° Bé.) are dissolved in 10 parts of water, and diluted with 150 parts of water. Five parts of this solution are diluted with twice their own volume of water, and the silk is entered in this bath for half to three-quarters of an hour, at first cold and then at 50° C., after which it is wound off. Finally, it is chromed in a 1 % solution of bichromate of soda and a little sulphuric acid, for half an hour, this treatment being repeated later.

TESTING DYED SILK FOR LOADING

We have already seen to what extent the loading of silk is practised, and also that, in some methods of dyeing, —*e. g.* mordanting the silk with metallic salts and then dyeing with mordant dyestuffs—a modest and unintentional, but inevitable, amount of loading is produced. No objection can, of course, be raised against this kind of loading, or indeed against intentional loading, so long as it is kept within certain limits, and can be justified or excused on technical grounds. Such objection only commences when the loading is practised for selfish ends, in order to make money out of an intentional deception of the public; in other words, when the loading is fraudulent. Whether there is really any deception is a point that can only be decided by chemical examination, and in this connection it is necessary to discriminate between coloured and black silks.

Testing Loaded Coloured Silks.—Several methods may be adopted, the simplest and most reliable being to boil the sample of silk 2–3 times in distilled water, which will, in certain circumstances, extract sugar, sulphate of magnesia and Glauber salt. Sugar is tested for by boiling Fehling solution and pouring into it the previously acidified (with HCl) extract, also at boiling temperature. If the Fehling solution is decolorised, and a red precipitate of cuprous oxide form, sugar is present. Any sulphate of magnesia accompanying the sugar loading is detected by ammonium phosphate, and any Glauber salt by barium chloride. The insoluble loading agents are detected by incinerating the boiled and washed silk in a platinum crucible, weighing the ash after cooling, and treating it with hot concentrated, chemically pure hydrochloric acid. If the resulting solution gives a yellow precipitate with sulphuretted hydrogen, the silk has been loaded with tin. The quantitative determination of the amount requires the skill of the professional chemist. Bismuth and antimony salts—if used at all for loading—are also revealed by sulphuretted hydrogen, bismuth giving a brownish-black, and antimony an orange-red, precipitate.

If an examination for soluble loading agents is not required—that is to say, if only tin is to be tested for—the sample of silk is incinerated in a porcelain crucible with its own weight of caustic soda and a trace of saltpetre, the cooled melt being extracted with water, acidified with a little hydrochloric acid and tested with sulphuretted hydrogen as above.

Of late years, loaded raw silk has made its appearance in commerce, the chief loading agents being fat (up to 8 %, as compared with the natural 0·03–0·06 %), soap, glycerine and sugar. Fat is determined by extraction with ether, the raw silk being weighed before and after extracting and drying. The nature of the fat must be ascertained separately, after the evaporation of the ether. Mineral fats can be separated from organic fats by saponification, the latter being saponifiable, the former not. Glycerine is generally associated with soap, small quantities of which—originating possibly in the spinning process—may be disregarded. Glycerine, soap and sugar are found by treating the air-dry silk with distilled water. The total weight of the constituents insoluble in water is estimated by weighing the raw silk before and after extracting it with water; or this treatment may also be practised after extraction with ether. An alkaline reaction of the aqueous extract indicates soap. To detect glycerine, the concentrated aqueous extract is acidified with dilute sulphuric acid—which destroys any soap present—followed by filtration, the sulphuric acid being then neutralised by an excess of barium carbonate. The liquid is then evaporated to dryness and the residue treated with ether-alcohol, to dissolve out any glycerine present, which, on evaporating the extract, remains behind as a syrupy, non-drying residue, which should give the characteristic acrolein reaction.

Sugar is detected with Fehling solution, as already described.

Testing Loaded Black Silk.—This examination is naturally more difficult, the number of loading agents being far greater, and is generally conducted on the following lines: The moisture content is first determined by drying the sample of silk, preferably in the conditioning apparatus (*q. v.*). The silk is next boiled in distilled water, in the same way as coloured silks, the aqueous decoction being tested for sugar, glycerine, sulphate of magnesia and Glauber salt, as above. Instead of direct incineration, black silk is first treated with ether or benzine, for which purpose it must first be dried and weighed. After the ether treatment, it is re-weighed, the loss giving the amount of substances soluble in ether or benzine (viz. fat, wax, paraffin, etc.) added to waterproof the fabric in finishing. The ethereal extract is concentrated and treated for about half an hour with lukewarm, pure, dilute (1 : 2) hydrochloric acid. If the black silk turns reddish-yellow, and the acid dark brown (which does not turn violet on addition of limewater), the silk has been loaded with iron and tannin. The yellowish coloration of the fibre is due to tannin; and from the colour, a skilled analyst can predicate, with a fair amount of certainty, the kind of tannin used: whether gallnut, sumach, chestnut extract, cutch, etc. If, on the other hand, the foregoing treatment leaves the acid coloured red, which turns violet with limewater, the silk has been dyed with logwood.

If the acid treatment leaves the silk dark green, and the acid yellow without any change to violet on addition of limewater, Berlin blue has been used, *i. e.* the black has been grounded with Berlin blue. The hydrochloric solution contains any salts of iron, chromium and alumina present, and these can be identified by the usual tests.

The silk from the acid treatment is well washed, and then treated with a boiling alkaline solution, which will extract any Berlin blue and most of the tannins, which can be detected by the addition of ferric acetate. If the examination is confined to detecting the presence of tannin (leaving soluble loading ingredients out of the question), the silk is treated for half an hour with a weak, boiling-hot solution of carbonate of soda, filtered, and the filtrate neutralised with acetic acid. If tannin loading has been practised, the filtrate turns blackish-blue to black on addition of ferric acetate, and blackish-green in presence of cutch. If no special importance is attached to the detection of fat and tanning agents, the silk may be incinerated after boiling, the residue being taken up with hot, concentrated hydrochloric acid, and the metals identified in the manner already given. The foregoing reactions will furnish an approximate idea of the quantitative composition of the dye and loading, and longer experience will enable a fairly accurate conclusion to be drawn.

If the examination be extended to the dyestuff fixed on the fibre, the matter becomes far more complicated, and the reactions of the dyestuffs on the fibre must be taken into consideration, which, however, is far outside the scope of the present work.

Colour-dyeing

This branch comprises the production of all shades except black, and does not call for much remark, the dyeing process being extremely simple when only single dyestuffs are in question, though it becomes more difficult when several are used in combination. In the latter case, it is by no means a matter of indifference whether the dyestuffs are used together or in succession, the results being not at all the same. Here the characteristic phenomena of capillarity come into operation, both in the longitudinal and transverse directions. The capillary conductivity differs for each dyestuff, *i. e.* the solution of one dyestuff penetrates the fibre more easily or with greater difficulty than that of another. This is very clearly shown by suspending a hank of silk in a solution containing several dyestuffs: one of them will ascend higher than another. In these circumstances, three zones are usually formed, the top one showing the more readily absorbed dyestuff, the bottom one the less readily absorbed, and an intermediate zone of mixed shade. The same zonal character is also found in the penetration of the fibre, when a cross section of the dyed silk is examined under the microscope. If such a differentiation into zones occurs during the simultaneous application of several dyes, it will naturally be still more accentuated in successive dyeing, *i. e.* the dyestuff last used will occupy the outer zone and thus mask the preceding dyestuff. Translated into practice, this means that the dyestuff used for bottoming will be found more towards the centre of the fibre, and the topping dyestuff more on the surface. The bottoming dye is seen better on looking at and through the fabric, the topping dye by viewing it sideways. The divergent imbibition properties of the dyestuffs are probably one of the causes of variegated dyeings.

In combining several dyes it is highly important to select such as have as nearly as possible the same properties—and consequently the same affinity for silk—and are taken up by the fibre at approximately the same temperature. The non-observance of this precaution is a further cause of variegated dyeings.

The various shades of colour are usually divided into pale (light), medium and dark, which can, of course, be obtained from one and the same dye, used in different quantities.

Light shades include white, ivory, cream, flesh tint, pink, sky blue, maize and apple green. Of course, it is incorrect to speak of " dyeing " white, this being obtained by bleaching the silk. Even the best white, however, has always a yellow tinge, which must be suppressed ("killed"), in order to obtain a pure white, by the addition of the complementary colour—in this case violet—preferably with mauveine and rosolane. The simplest way to produce ivory and cream is by chrysophenine—which is fast to light—or with quinoline yellow. It is always advisable to use only dyestuffs that are the fastest to light for pale shades. In addition, plenty of bast soap should be used, and the goods entered at low initial temperatures, in order to prevent uneven dyeing. Flesh tint and pink are obtained with rhodamine or azofuchsine; delicate salmon pink with auramine and rhodamine. Victoria blue is usually recommended for sky blue, but is far too fugitive to light; and it is better to use alkali blue or brilliant acid blue B.

Medium and dark shades present not the slightest difficulty, so long as only single dyes are used. A whole series of dyestuffs for all shades of red, orange, yellow, green, blue, violet and brown, have already been given in an earlier section. The primary colours dye easily and satisfactorily, and also the first series of compound-colour dyestuffs (binary colours) can be produced in nearly all shades from commercial dyestuffs, without combination.

The ternary colours, too (that is to say, those produced from a primary colour combined with a binary colour—such as red with orange, blue with green, or yellow with green—and form transition shades between one of the colours of the spectrum and its neighbour), are to be found among the innumerable marks of the dyestuff manufacturers. On the other hand, combinations of dyestuffs that are not consecutive members of the spectrum, such as red with green, orange with blue, yellow with violet, cannot be obtained from any commercial dyestuffs. Here begins the enormous number of possible shades, which must be *seen*, since no scientific names have yet been invented for them; and here, too, begins the predominance of the shades produced in practice, and of the specimen books; and to some extent even the recipes, which, however, are only valuable to the dyer who has given due consideration, not only to the quantities of dyestuff prescribed, but also to the working conditions laid down in the accompanying instructions.

To this category belong, first of all, the various shades known as mode colours and greys, for which no names are to be found in any living language. Even such current terms as myrtle, moss green, lavender, reseda, olive, heliotrope, mallow, etc., which should really denote a fairly well-defined shade, are quite indefinite. To realise this, one has only to compare the beiges, heliotropes, silver greys, resedas and myrtles turned out by a hundred different dyers. In fact, the author is certain that, out of a hundred specimens, hardly two would be found an exact match—a proof that each dyer has a different idea of what a given term conveys. To go more closely into this subject would bring us to the highly interesting domain of the theory of colour, which is even now debatable ground.

The production of mode colours and greys by combining several colours is one of the most difficult tasks of the dyer, and necessitates, above all, considerable experience and a skilled eye. The surest way to achieve success is by bottoming with a basic grey—*e. g.* new fast grey—that dyes uniformly, and then shading according to requirements. If blue predominates, a pale bottoming can be obtained with Victoria blue, and shading. There are no generally applicable prescriptions or rules for the operation.

Colours are dyed on both loaded and unloaded silks. In the former case tin is the only permissible loading agent for pale and medium shades. The best dyestuffs to use are the basic dyestuffs, fast to washing, acid dyestuffs of equal fastness, or the corresponding benzidine series. The basic and benzidine dyestuffs are used in a bast-soap bath soured with acetic acid; the acid dyestuffs in one soured with sulphuric acid; for example: red with diamine scarlet B; elder with heliotrope BB; the tin-loaded silk being entered, the bath being raised to the boil, and 200–300% of sumach extract added, according to the degree of loading required. The silk is left in the bath till cold. If the shade does not match the pattern, the silk must be shaded *before* loading with tannin.

In proportion as darker shades are to be produced, loading with iron and cutch can be employed, and this brings us into the neutral zone between colour-dyeing and black-dyeing, namely the production of loaded colours, fast to water, such as are required for umbrella fabrics and dress goods. Here again we get into the unscientific and purely empirical methods already described in connection with black-dyeing. A rational, systematic method is entirely lacking; iron bottoming, soap baths, cutch baths, stannic chloride solutions, Berlin blue, etc., being arbitrarily employed, and, after sufficient loading and darkening, dyeing with logwood, fuchsine, tumeric, cutch, or the like. In some cases, when it is desired to be quite up to date, acid fuchsine, acid brown, acid violet, fast green, methyl violet, etc., are resorted to. In fact, dyeings of this kind are still largely carried out in practice; but as they have been described in standard works, they cannot be omitted from mention here, although they are not in accordance with the present state of the art, and the same results, if not better, in respect of fastness, can be obtained by newer methods.

Brown for Pure Silk (Slightly Loaded).—According to the loading desired, the silk is given 2–3 iron bottomings with basic ferric sulphate (30° Bé.), fixed in a boiling soap bath, and centrifuged without rinsing. It is next dyed with 300 % of cutch, 3 % of fuchsine, turmeric and logwood, according to shade, being entered at boiling heat and left to draw for a day; after which, 2 % of tin salt is added and the goods left for another half-day. When taken out, they are washed, and then entered in a soap bath soured with sulphuric acid, followed by a good washing, and brightening with acetic acid and oil.

Ordinary Brown on Pure Silk.—The silk is bottomed as above, then entered in a fresh cutch bath (10° Bé.), and in an old one (7° Bé.). After being left to draw for three-quarters of an hour, the silk is dyed with safranine, acid fuchsine or other aniline dyestuff.

English Brown for Souple Silk (Heavy Loading).—The silk is suspended in a boiling-hot bath of 50 parts of cutch (for 10 parts of silk) and 0·09 of fuchsine, where it is worked about for two hours and left all night. If not then sufficiently softened, 1·66 parts of tin salt and 3·33 of ferrous sulphate are added, and the material treated for one and a half to two hours at 80° C. It is next well washed, and entered for thirty-six hours in a 15 % soap bath, being worked round 3–4 times during that period, and is then entered into a bath containing 5 parts of cutch, with fuchsine and logwood according to requirements, where it is treated for one hour, taken out and 0·1–0·15 part of chromate of potash added to the bath liquor. When this has cooled down to 50° C., the silk is entered again, and warmed until the correct shade is attained. The operation is terminated by washing, and brightening in the same way as for brown on pure silk.

Russian Green on Pure Silk (*Par Loading*).—The silk is bottomed as in the case of brown, and then dyed in a soda bath with 10–15 % of alkali blue, in which it is left until the ground colour is sufficiently dark, after which it is rinsed, and the blue is developed in a sulphuric acid bath. Washing is followed by shading in a bath of about 100 % of cutch or turmeric, logwood being added as required, the silk being left until the bath has cooled down to about 40° C., and then fixed, in the same bath, with about 3 % of tin salt, this quantity being slightly increased if the ground-colour is too dark. After remaining an hour in this bath, the silk is washed, and brightened with acetic acid and oil. The shade can be modified as desired in the last-named bath by adding tartaric acid, logwood and fustic. In the case of shades for which the dull green of the iron catechutannate is unsuitable, the cutch must be replaced by gallnuts or sumach.

Carmelite Grey on Pure Silk (*Loading* 25 %).—The silk is bottomed one or more times with basic ferric acetate (30° Bé.), then boiled with 45 % of soap, and dyed, in the same bath, with a methyl violet-red tinge. After washing, it is treated, either with China gallnuts or, *e. g.*, with 65–70 % of sumach extract, the temperature ranging from medium up to 90° C. according as the final shade is to be light or darker. The silk can also be dyed, in the same bath, darker with more methyl violet, or shaded with a methyl violet of redder or bluer tinge. It is left to cool in the bath, because most of the tannin is taken up by the silk in the cold liquor. Finally it is washed and brightened as above. Methyl violet may be replaced by rosolane or fast acid violet.

Tobacco Brown on Slightly Loaded Pure Silk.—After one or more iron bottomings, fixed with boiling soap, the silk is dyed with 3% of induline, 12% of Indian yellow and 1–2% of diamond scarlet, in a bast-soap bath soured with sulphuric acid. After boiling up the bath, 200% of sumach extract is added, the silk being worked about 15–20 times, washed, soaped in the cold with 12–15% of soap, washed, and brightened with 2% of sulphuric acid.

Navy Blue on Pure Silk (Par Loading).—The silk is bottomed once with iron, and then blued with 15% of yellow prussiate and 25% of hydrochloric acid, at 50–55° C.; after which it is entered in a bath of 25% of gall-nut extract and warmed to 45–70° C. according to the shade desired, being finally washed, and brightened with acetic acid and oil.

Umbrella Green on Souple Silk.—The operations comprise 1–3 iron bottomings; bluing; soupling with divi-divi (with or without tin salt); dyeing in a fustic bath at 50–80° C. according to depth; washing; topping (when tin salt is used) in an old logwood bath with addition of soap; washing, and brightening.

Navy Blue on Souple Silk.—The silk is bottomed 1–3 times with iron; blued, and dyed with a decoction of China gallnuts and acid violet, the bath being gradually raised to the boil, then allowed to cool down to 60° C. and treated with tin salt. Topping in an old bath of logwood and soap follows, and the silk is finally washed and brightened.

All the above shades can be matched, with at least equal fastness and no more expense, besides more simply and quicker, by means of alizarine dyestuffs, though not with the same degree of loading. Consequently, if the old method is still employed, one must conclude that the maker attaches more importance to loading than to colour.

DYEING CHAPPE SILK

Chappe silk is first wound into 70 grm. hanks, tied with cotton, and is then cleansed by entering in a boiling bath containing 25 % of soda crystals (based on the weight of the silk), where it is worked round 5 times, then washed with water at hand temperature, entered for one and a half hours in a boiling-hot bath containing 20 % of Marseilles soap, and rinsed; which done, it is ready for dyeing.

Before, however, proceeding to this next stage, it must be ascertained whether the silk is to be woven by hand or in a power loom, because silk for hand weaving must have "scroop," whereas for machine weaving it must be soft, since otherwise the plough could not cut evenly.

The softening of chappe silk requires, above all, a proper softening mordant, to ensure the threads being supple and not sticky. The mordanting liquor is prepared by filling a clean pan, holding 300 litres (66 galls.), two-thirds full with boiling water, to which 15 kilos. (33 lb.) of anhydrous alum are added, followed by the gradual addition of 3½ kilos. (7¾ lb.) of soda crystals, previously dissolved in water, then by 1½ litres (0·33 gall.) of acetic acid and ¾ litre (0·055 gall.) of olive oil. The whole is boiled, and well stirred, for three-quarters of an hour, then cooled, and the clear liquor drawn off.

Chappe for hand weaving is dyed in exactly the same way as silk, as is also that for weaving in the power loom; but, in the latter case, the dyed hanks, after being brightened, are rinsed and entered in a fresh bath of cold water containing 20% of acetic acid and 70% of the above softening liquor (more for dark colours), in which it is worked 5 times, centrifuged, stretched, beaten, dried and stretched again.

If, after this treatment, the chappe is still sticky and feels more or less stiff, it is preferably entered in a bath of Marseilles soap, with a good frothy lather, in which it is worked round 5 times, washed well and finally put through a bath of water soured with 1% of acetic acid, in which it is again worked 5 times. If this does not produce the required effect, a little softening liquor may be added to this final bath.

With regard to the choice of dyestuffs, it may be stated that, for hand weaving, the dyestuffs may be inferior in fastness to water than those for machine weaving. The dyestuffs are almost exclusively those belonging to the acid group (substantive dyes being now also used), whilst cutch, logwood and fustic are only employed for black, this being dyed according to the following recipes.

Ordinary Black (*Steinbeck*).—The chappe is entered cold, and worked a few times, in a bath of 10% of fustic extract, 1½% of copper sulphate and 6½% of ferrous sulphate being then added, and the silk worked 7 times; after which the temperature is raised to 85° C. for an hour. The washed chappe is dyed with 150% of logwood extract and 25% of soap, and is brightened with acetic acid, olive oil and size.

If a blue-black is desired without resorting to bluing, an alumina mordant is employed to produce the logwood-alumina lake, or else the chappe is bottomed with alkali blue as described below.

Blue-Black.—Mordant with basic aluminium sulphate, and dye with logwood as for ordinary black.

Blue-Black.—Dye with 6% of alkali blue B., entering in basic ferric sulphate (30° Bé.), and then in a cutch bath (2° Bé.), followed by rinsing, and topping with logwood and soap.

Deep Black, with Par Loading (*Steinbeck*).—The chappe is bottomed with iron (30° Bé.), rinsed, and dyed in a bath of 300 % of cutch and 30 % of logwood, being next darkened with iron pyrolignite (5° Bé.), returned to the old cutch bath, and topped with 100 % of logwood and 25% of soap. Brightening is effected in the same way as for ordinary black.

A few words may be said with regard to the dyeing of bourette silk, which is used for passementerie, chenille and silk nops in woollens. As a rule, no preliminary treatment is required, and the silk is dyed in a bath soured with acetic or sulphuric acid, without bast soap.

Special Effects in Silk-dyeing

Fluorescent (*Bronze*) *Dyeings.*—Some dyestuffs possess the property of imparting a strong fluorescence to silk, especially the phthaleine dyestuffs. The various eosines give either an orange to scarlet effect when viewed from the front and yellowish when looked at sideways, or else bluish-red and scarlet respectively, whilst uranine gives a beautiful greenish-yellow fluorescence. "Bleu fluorescent" dyes silk a bluish-violet with red fluorescence, naphthyl blue doing the same. The fluorescence of all these dyestuffs is retained when they are combined with others, provided basic dyestuffs of high covering power are avoided, as well as dark shades. The most usual practice is to bottom with "bleu fluorescent" and top with other dyestuffs, thus retaining the red fluorescence whilst producing a different colour in frontal aspect. Another method is to bottom with eosines and rhodamines, and top with other faintly acid dyestuffs. A greater variety of similar kind is obtained by dyeing for shot effects.

Shot Effects are secured either on the basis of the foregoing methods by bottoming with a not too light-coloured dyestuff and topping with a second of decidedly different colour, taking care, however, that the topping layer is very thin, so that the ground-colour can be clearly discerned through it from the front, whilst only the former is visible from the side. Effects of this kind are obtained, for instance, with a brown ground topped with green, or dark blue ground topped with yellow.

Two-Colour Dyeings presuppose the presence of two different qualities of silk in the fabric, which behave differently towards different dyestuffs; or mordanted and unmordanted silk, each of which can be dyed with a different dyestuff, according to the methods of Lange or Zillessen.

Ombres.—Shaded effects on hank silk are obtained by binding the hanks firmly on rods, using only a small amount of dyestuff in the bath, filling the latter quite full of liquor, warming it slightly, and leaving the hanks in suspension without working them about. After a time a certain quantity of the bath liquor is drawn off, replaced by a smaller amount of dyestuff solution, and the hanks again left to draw for a while. This treatment can be repeated several times, the hanks being left in the bath all through; and finally the hanks will be found correspondingly shaded, from a pale shade, or even white, at the upper end and deepening progressively downwards. Similar results can be obtained by leaving the bath full all the time, and raising the hanks a little out of the liquor, by means of a suitable frame, each time it is replenished with dye.

Jaspures are watered effects, in which parts of the yarn are left undyed, giving results similar to those obtained by yarn-printing. The parts to be left white are tied round with some waterproof material, and the hanks are held on two sticks and dyed in strong liquors.

Dry Dyeing.—This contradictory name implies that the silk is dyed in a solution of the dyestuff in benzine instead of water. The special dyestuffs used for this purpose are prepared according to the Boursier & Boissel, Holliday or Petitdidier Patents, and are sold as aniline-fat dyes, resinate dyes, benzinidene, etc., dyestuffs. They are mostly derived from basic dyestuffs, and are prepared by precipitation with solutions of soap or rosin, the dye preparation being separated by means of sulphuric acid. They are soluble in fats or oils, but more effectually in benzine. Of course, dyeing in a benzine bath is not an operation that can be suitably carried out in regular dyeworks; and, as a matter of fact, it is confined to works where garments are dyed, in which the operatives are accustomed to working with benzine and where the rapid dyeing of silk garments in light colours is in question.

Dyeing Silk in the Piece

At one time, silk was dyed solely in the hank, piece-dyeing having only been introduced during the last twenty years or so. The practice is growing, but has by no means attained the same importance as in the case of woollen and cotton fabrics. At first, piece-dyeing was confined to silks which would not be strong enough to stand weaving if first scoured and dyed, though quite suitable in the state of raw silk. Fine, delicate fabrics like barége, etc., were also piece-dyed. At present, however, even heavy piece goods are dyed, though not in all cases.

In point of the selection of dyestuffs and the method of dyeing, there is no difference between piece- and hank-dyeing, though the preliminary treatment differs. Fabrics woven from raw silk must be scoured in the same way as hank silk, and scoured fully, though not usually loaded. The dyeing is performed in wide vats which will take the fabric in the wide-open condition, or else a double jigger is used. In this case the wide-open piece is wound on one of the rollers, mounted on long arms on either side of the apparatus, the free end of the fabric being passed between a pair of squeezing rollers and then over various guide rollers through the dye vat, on leaving which it goes through another pair of squeezing rollers and is wound on to the second winding roller. In this way the fabric takes a sinuous course through the dye liquor.

By reversing the machine the piece can be wound off the one roller and on to the other as many times as desired, passing through the dye liquor in the prescribed manner each time, wide open.

After dyeing, the piece is rinsed in the jigger itself, and may also be gummed in the machine, from which it passes direct to the finishing and drying machine. This consists of a large copper (usually tinned) drying cylinder, together with large gumming pads with adjustable facing and glass or brass doctors. The machine can be run at varying speeds by means of spur gearing and friction drive, and it is usually arranged in such a way that the gummed side of the fabric does not come in contact with any guide rollers until quite dry.

MATCHING

The dyer's art attains its culminating point in matching, *i. e.* dyeing to the exact shade of a sample supplied. This is more difficult than actual dyeing, and entails long experience and a practised eye. The matching of silk presents special difficulties by reason of the peculiar behaviour of the fibre towards light rays, some of which it absorbs, the others being reflected. It is to this circumstance that the lustre of silk is due; and, in turn, it confuses the dyer's eye and makes the appreciation of the true colour more difficult. Nevertheless, matching is still a comparatively simple matter when the specimen for comparison is also of silk; and it only becomes really difficult when the pattern is of a different material, the problem being still further complicated when the dyer is expected to produce a shade that will match the sample perfectly both by daylight and artificial light.

The first rule in matching is never to compare the still wet dyeing with the dry sample. Previous to doing this, a few threads at least must be dried, preferably by wrapping them in a handkerchief or clean white cotton cloth and laying them on a steam-pipe. When dried, the silk should be laid on a sheet of white paper side by side with the sample, and the difference in the shade should be noted as quickly as possible, so as to be able to estimate the direction in which shading is needed.

The second rule is to compare and judge the shades always in a north light. If there is no window on that side of the building, go out into the yard and face north.

Of course, the matching must be postponed until the desired shade is nearly attained. It is, however, extremely difficult to teach matching by verbal description, it being necessary to explain and demonstrate this delicate operation by practical object lessons. A special point for the beginner is that he should learn to judge shades by comparison, so that when he has a given colour to match, he may know whether the dyeing is too red, or too yellow, or too blue, in comparison with the sample to be matched, or whether one or the other of these primary colours requires to be added. A warning should be uttered against looking at the colours too long at a time, as this easily fatigues the eye, and finally confuses it to such a degree that a differentiation of shades becomes impossible.

Silk intended for plush must be viewed on the pile, as this often has quite a different shade from the surface of the silk. This type of matching, however, must also be learned by object lessons, and cannot be taught in books.

TESTING SILK-DYEINGS FOR FASTNESS

Before a silk dyer begins to execute an order, he must first make certain of what is expected of the dyed goods in respect of fastness, because upon this depends the choice of the dyestuffs used. These requirements, in turn, depend on the uses to which the fabrics are to be put; and it will be manifest that a silk which is to be used, *e. g.*, for umbrellas must fulfil different conditions from one that is intended for linings, curtains or barége. A short account of the usual requirements expected of silk as regards fastness will now be given.

Fastness to Water.—Silk intended for umbrella fabrics, or for effect threads in plain fabrics that are to be afterwards dyed, must be able to stand the action of water; that is to say, the colour must not change in any way, or wash out of the material, either in the rain or during the dyeing process. The tests for fastness are based on the following facts: Rain is almost chemically pure, distilled, atmospheric water, and therefore the dyed silk is plaited with a small skein of undyed silk and one of white cotton, and immersed all night in rain water—distilled water, however, being more convenient. Under these conditions the water should acquire no more than a very slight coloration, if any, and the white yarn must remain unstained. This water test is the most important for silk, and the one most frequently made. The basic and acid dyestuffs in general are not fast to water, in which respect they differ from all the mordant dyestuffs and most of the substantive and diazo dyestuffs, *e. g.* benzoazurine G, chrysamine, chrysophenine, primuline, etc. As a rule, the fastness to water is lower on loaded silks.

Fastness to Soap.—Goods that have to be washed at intervals, such as knitting silks or silken fancy threads, should not bleed when treated with soap solution. To apply the test, the silk is plaited with white silk and cotton and boiled for an hour in a solution of 10 parts of Marseilles soap in 1000 of distilled water. Mordant dyeings must only be treated for a similar time with a solution of 5 parts of neutral soap at 80° C. In most cases a little of the colouring matter will come out; but that is, of itself, no proof that the dyeing is not fast, the essential point being that the coloured soap liquor must not stain the white threads present in the sample. If a milder treatment is desired, the soap liquor is warmed to about 60° C. and the sample immersed for twenty minutes, then taken out, rinsed and left for twenty minutes in the rinsing water, returned to the hot soap bath, and repeating the whole operation as often as desired. The main point is that there should be no bleeding on to the white threads.

Fastness to Milling.—Silk intended for fancy threads in dress fabrics, and also loose, waste silk which is sometimes woven in cloth making, must also be able to stand milling. The plaited sample is placed for half an hour in a warm solution (50° C.) of 5 parts of Marseilles soap and 1 of carbonate of soda in 1000 of water, and well squeezed and rubbed during that period, after which it is left alone in the liquor for another quarter of an hour, and rinsed.

In this case, too, there should be no staining of the accompanying white threads.

Fastness to Acid is tested by applying 30% acetic acid with a pad. The colour should remain unaltered.

Fastness to Alkali is tested with 20% ammonia, in the same way.

Fastness to Light.—Testing for fastness to light is a rather problematical matter, and the most that can be achieved is to ascertain whether a dyestuff undergoes any change at all under the influence of sunlight or diffused daylight. The only way in which investigations of this kind can acquire any value is when an object of the same depth of shade, of known fastness to light, is taken as the standard of comparison. In carrying out the test, the specimen (yarn or fabric) under examination is mounted on a piece of board, and one half of it is then covered with a second board or suitable piece of millboard, the whole being then hung up in a window with a southern aspect and examined from time to time to see whether the colour shows any signs of fading. It should be noted that the fastness to light may differ considerably, according as the silk has been loaded or not.

Fastness to Topping.—This property must be possessed by silk dyeings which are to be woven as fancy threads or small patterns in woollen fabrics, and consequently having to stand the subsequent dyeing of the fabric with acid or mordant wool dyestuffs in the piece without becoming stained. This condition is fulfilled by most of the diazo dyeings.

Fastness to Boiling.—Dyed silk for fancy threads in woollen fabrics that are to be dyed in the piece must stand boiling without the colour bleeding or suffering more than a slight alteration in shade. The best way of applying the test is by plaiting a specimen with white silk or cotton and lightly boiling the resulting tress for an hour in a 0·5 % solution of neutral soap, or in pure water only. In the case of mordant dyestuffs, the boiling should be continued for another hour, without the shade or depth of colour suffering more than slight alteration.

Fastness to Bleaching.—This property is required of silks that are to be woven with other textile fibres that will be afterwards bleached, or treated with hydrogen peroxide. The silk to be tested is plaited with raw silk and white cotton, and after being treated for one and a half hours at 90° C. with 60 % of Marseilles soap, is entered in a boiling-hot solution of 300 parts of hydrogen peroxide, 700 of water and 3 of ammonia, in which it is left to cool all night, and after souring with sulphuric acid, is rinsed. Most of the vat dyes will stand this drastic test.

Fastness to Sulphur.—This is required of silks that are to be woven into woollen fabrics which will be sulphured. The colour must not change or stain the wool.

Treatment of Silk after Dyeing

Whereas, in the case of other textile fibres, dyeing is only followed by rinsing and drying, silk has to be put through several other treatments, partly of a chemical nature and partly mechanical. These are necessitated to some extent by the character of the silk fibre, and also by the practice of dyeing the silk in a soured bast-soap bath, and are therefore characteristic. The soured bast-soap bath is a kind of emulsion containing the sericin and the fatty acids of the silk in a state of extremely fine suspension. On issuing from this bath the silk has apparently lost its lustre and feel, and the colour is dirty and dull. To restore its pristine lustre requires an after-treatment or brightening, which may be effected in various ways. The most usual method is to enter the silk in an acid bath, generally sulphuric or acetic acid, though, for special purposes, tartaric or citric acid is employed. The choice of acid depends on whether it is merely desired to improve the colour and lustre of the silk, or to impart the "scroop" which many authors assert to be characteristic of silk fibre, but which it does not, a priori, possess. The best way to develop this peculiarity is with tartaric or citric acid, though boric acid produces similar results. For loaded silks, a larger quantity of acid is required. If, on the other hand, the silk is to remain soft, it is brightened with basic alum or basic aluminium acetate. The softening mordant employed in preparing chappe silk for the power loom is nothing more than a combined brightening process with basic alum and oil. Oil is used more particularly on loaded blacks, to soften the fibre and increase the lustre. For this purpose, olive oil is made into a kind of soap (or at least an emulsion) by warming it along with its own weight of carbonate of soda and thrice that quantity of water. The process is therefore merely one of brightening with soap, the softening effect of which on fibres and fabrics is generally known. In practice, the soap emulsion is sometimes replaced by Turkey-red oil, or fuller's earth. If, on the other hand, it is desired to bring out the peculiar scroop of silk, tartaric or citric acid must be added to the soap emulsion.

The use of hydrochloric acid should be discountenanced, since it has a bad effect on many colours. Black is the only one on which it can be used without risk.

The composition of the brightening baths may vary considerably according to the effect to be produced and the character of the silk to be treated. The bath temperature must also be modified to correspond, being lukewarm for soft silk and hard silk. If the object is merely souring, with or without an addition of oil emulsion, the temperature may be raised to 35 or 40° C.; but the operation is not infrequently performed in the cold. The silk is only left a short time in the bath, in which it is worked round 5–6 times, and then wrung, without rinsing, and dyed. For soft brightening, the wringing is omitted.

The brightening baths are often used for shading at the same time, a readily distributing dyestuff being added—or sometimes even very finely levigated Berlin blue—to improve the existing shade.

Finally, brightening is combined with dressing, in which case a solution of fats, oils, paraffin, wax, etc., in benzine or benzole, is employed. This is particularly the case with heavily-loaded black silks, in order to coat them with a film of paraffin, etc., as a protection from the air. Highly-loaded silks are also frequently sized as well. Taken altogether, brightening may be also regarded as a kind of finishing process.

Another after-treatment, which, however, has nothing to do with brightening, is the after-tanning already described in connection with dyeing with basic dyestuffs (*q. v.*). In addition to the recommended treatment with tannin and tartar emetic, Steinbeck proposes to make dyeings with basic dyestuffs fast to water by treating them in a bath (at 25° C.) containing 10% of cutch, or of sumac or gallnut extract. In this bath the silk is worked round 5 times, well rinsed and then entered in a bath of $\frac{1}{3}$% of tin salt dissolved in $2\frac{1}{2}$% of acetic acid, where it is treated for half an hour and is afterwards brightened with 2–3% of size, acetic acid and oil. This treatment is unsuitable, so far as cutch is concerned, for light shades.

The mechanical after-treatments include drying, stretching, smoothing and lustring, all of which have been described already, together with the machines adapted to be used for this purpose.

GILDING SILK

Attempts have not been lacking to gild silk fibres, and success has been achieved, though in a very roundabout and expensive manner. This applies particularly to the oldest method of Gonin, who impregnated the silk with gold solution, then deposited metallic gold by reduction, and finally polished the silk—a method which entailed a useless waste of gold salt, because it is quite sufficient to gild the surface of the silk. This can be done by electroplating, but the existing methods adopted seem all to be too complicated to be suitable for general application, since, as silk is a bad conductor of electricity, it must first be rendered conductive, as well as being made impervious to the electrolyte. It is therefore unnecessary to pursue the subject further, more particularly as no dyer will ever be in a position to gild silk. The author is also of opinion that the newest method of producing metallised threads will also lead to a simple process of coating silk with gold. This method consists essentially in impregnating the fibre with a solution of cellulose acetate, and then applying the powdered metal (in this case gold) by mechanical means. The author is, however, unaware whether this method has yet found any practical application.

CHAPTER II

TUSSAH

Tussah Silk and its Properties.—Out of the numerous kinds of wild silk known, only five have become of any widespread interest, viz. Ailanthus silk, ricinus silk, Fagara silk, oak silk, and Tussah silk. The larvæ of the first three are cultivated on a large scale in India, Bengal, China and Japan; those of ricinus and oak silk occasionally in southern Europe as well. The moth (*Antheræa mylitta*) which spins tussah silk, however, cannot be cultivated. It is indigenous in India and Bengal, as far as the higher altitudes of the Himalayas, and also in southern China, where it feeds on the leaves of the jujube tree and certain varieties of oak. Tussah silk is the only member of the above series that has been able to make its way as a commercial article. It is sold both in the form of hanks and also as tissue, in large quantities, and will be known to many readers under its trade name of bast silk.

According to O. N. Witt, the cocoons of the tussah moth are about four times as large as, and much harder than, those of the ordinary silkworm, measuring 40–45 mm. in length by 25–30 mm. in width. They consist of a continuous double filament, about 1400 metres long and weighing 2–3 grms., which is easily unwound now that it has been discovered that the cementing medium (almost entirely composed of sodium urate), with which the whole cocoon is impregnated, can be dissolved by alkaline liquids. The yield of silk fibre is about 30% of the total weight of the cocoon. The cocoons are frequently shipped to Europe for treatment, the tussah fibre prepared in India failing to meet the requirements of the European market. A kind of tussah chappe is spun from the waste of the tussah cocoons, and is much sought after for making plush, imitation pelt and fancy fabrics. At one time, difficulty was experienced in using tussah silk because the natural brown colour could not be got rid of.

Chinese tussah is identical with the above-mentioned oak silk, which is spun by an oak moth (*Antheræa pernyi*). It differs from Indian tussah by its greyish-brown colour, greater fineness and absence of lustre.

Tussah silk[1] is, like true silk, a double filament, but whereas the latter is devoid of air passages and has a perfectly smooth, homogeneous outer surface, tussah silk contains air ducts and exhibits decided longitudinal striation. The diameter of tussah silk is nearly double that of true silk, averaging 45 by 24 μ. A characteristic feature of tussah fibre is the flattening of the filaments at the points of intersection on the cocoon, a peculiarity which is not found in mulberry silk. Moreover, in contrast to the latter, the cross section is flatter and ribbon-like instead of round. On the other hand, it has a higher and more vitreous lustre, when scoured, than true silk. The colour of tussah is brown to greyish-brown, whilst that of mulberry silk is yellow to white.

Chemically, tussah silk consists of fibroin and the cement which binds the individual filaments together; it does not contain any true sericin. Furthermore, the fibroin of tussah is not the same as that of mulberry silk. The so-called "bast" of tussah consists of substances (mineral salts, tanning agents, etc.) which the fibre absorbs from the water in reeling, and to which the brown colour is also due. Tussah contains considerably more mineral salts than true silk, both in the raw state (2·5–3·2 %, as compared with 0·9–1·5 %) and in the fibroin (0·5–1·5 % against 0·2–0·35 %). The chemical behaviour of the two kinds is fairly similar, tussah offering, in general, a greater resistance to chemical agents, such as alkalis; and it is only soluble with difficulty in zinc chloride and ammoniacal copper oxide. They differ also in their behaviour towards dyestuffs. When tussah silk is boiled in water, the vegetable substances absorbed from the reeling water are redissolved, and the solution gives the characteristic reactions for tanning. Tussah fibroin is richer in oxygen, but lower in carbon and nitrogen, than true silk fibroin. Another noteworthy feature is the different behaviour of tussah towards soap, which seems to combine with the cement—at least the tussah becomes more adhesive when treated with soap, and no bast soap is obtained. There are, however, commercial tussahs which will stand soaping without becoming agglutinant.

---

[1] With regard to the name tussah it should be mentioned that this is, of course, primarily applicable to the silk from *Antheræa mylitta*; many authors have extended it as a generic term covering all the wild silks.

According to von Höhnel, the best method of separating true from wild silk is with a cold-saturated solution of chromic acid diluted with an equal volume of water, the true silk alone being dissolved. A moderately strong solution of caustic potash gives the same results. Towards dyestuffs, tussah silk behaves in a characteristic manner, its absorbent properties, when scoured, being not inconsiderably greater than those of true silk; many dyestuffs are taken up with great avidity, and the dyebaths are sometimes completely exhausted in a few minutes.

SCOURING, BLEACHING AND LOADING TUSSAH

In the absence of bast, in the true sense of the term, it is hardly accurate to speak of removing bast from tussah. On the other hand, the bast is replaced by a cement composed mainly of sodium urate, a tannin that has been modified by oxidation, a gelatinous substance and a wax-like fat. This cement, whilst holding the filaments together, does not enclose them as a sheath, but permeates the whole fibre, and is frequently referred to as "bast." It is removed by boiling in water containing 10 parts of soda crystals, or 5 of calcined soda, per 1000, the bath being kept at boiling temperature for an hour, but without actual ebullition. The bath liquor takes up the brown colouring matter permeating the fibre, as well as the cementing material, and turns a dirty brown. If a second parcel of tussah be boiled in the same bath, the brown colouring matter is taken up by the fibre and darkens its colour, 2–3 thorough washings being then needed. A solution of water glass, with a very small addition of caustic soda, may also be used. When the boiling is finished, the tussah is treated in a boiling-hot bath containing 10–15 % of soap, and when washed is ready for bleaching or dyeing. Of course the brown-coloured bath liquor cannot be used as "tussah bast soap." Wild silks composed of very fine filaments or containing very little "bast" may also be boiled direct with soap, but must afterwards be completely freed from soap by treatment with acidified water, or preferably with dilute ammonia, since the presence of even small quantities of soap would impart a grey tone to the silk. Moreover, the boiling process can be omitted for many purposes. Boiling with dilute caustic soda also gives good results, but does not seem, as yet, to have been very largely employed.

Bleaching Tussah.—The natural pigment of tussah is quite different from that of true silk, being a tannin that has been altered by oxidation and cannot be eliminated by sulphuring. Its extraction necessitates the use of powerful oxidising agents, such as hydrogen peroxide, sodium peroxide or perboric acid.

Bleaching with hydrogen peroxide is effected in the following manner: A bleaching bath is prepared from 20–30 litres of hydrogen peroxide (containing 12 % by volume of H_2O_2), 800–1000 grms. of water glass, 500–600 of (previously dissolved) white soap, and 100–120 litres of water. The tussah is entered over-night, and next morning the bath is warmed to 60–80° C., the silk being worked about in it at intervals. The bleaching is followed by souring in fresh water containing a little sulphuric acid, and washing in cold water. According to another recipe, 60 litres of boiling water, 20 litres of hydrogen peroxide and 1½ litres of water glass, are taken to 10 kilos. of tussah, the material being worked round 4 times, left covered up for three hours, raised to the boil, worked once, left for another three hours, well rinsed, and soaped boiling hot. Hydrogen peroxide baths can be kept for further use, preferably in a cool, shady place, protected from air. They must also be slightly acidified.

In bleaching with sodium peroxide, 1·350 parts of commercial sulphuric acid are carefully run into 100 parts of cold water, 1 part of sodium peroxide being strewn in with continued slow stirring. The solution is made faintly alkaline with a little water glass (so as to blue litmus paper), and the tussah is worked about in it for half an hour in the cold, this being repeated at 50–60° C., after which the temperature is slowly raised to boiling point. The liquor should be examined again to see if it is sufficiently alkaline, and a little more water glass added if necessary. From time to time the bath is again raised to the boil, the tussah being left in for six to eight hours, or over-night. Finally, it is rinsed twice with fresh water, soured in a weak bath of sulphuric acid, and afterwards rinsed twice with cold water. The final treatment consists of soaping in a boiling-hot bath containing 5 parts of Marseilles soap per 1000 of water, succeeded by rinsing.

To obtain a fuller bleach, the above-named quantities of reagents are increased, 2 parts of commercial sulphuric acid and 4½ of sodium peroxide, for example, being taken per 100 of water; whilst for a lower degree of bleaching, the quantities may be reduced to one-half or two-thirds. In any event, a certain amount of caution is necessary, the dilute sulphuric acid being prepared first, and only adding the sodium peroxide, in small portions, when the liquor is quite cold. The addition of the further ingredients is postponed until just before use. The bath can be employed over again for a considerable time. The proportions of the bath are 1:30. Silbermann gives the following instructions: 100 parts of boiled tussah, carefully freed from soap, are entered in a bath of 2500 parts of water (at 30° C.) and 90 % of sulphate of magnesia (free from chlorine), in which it is worked several times and then lifted. Next, 25–30 % of finely-powdered sodium peroxide are carefully added, in small portions. After the effervescence and heating which ensue each time, the liquor is stirred and the tussah is re-entered and worked round, the bath being then slowly raised to 80–95° C. At the end of one and a half to two hours the operation will be complete, and the tussah is lifted out of the liquor which is now milky from the precipitation of magnesium hydroxide. The liquor is cleared by an addition of sulphuric acid, and the silk, after being worked round again, is well washed. Finally it is soaped for an hour in a boiling-hot soap bath, and afterwards washed.

In practice, the scouring and bleaching of tussah are frequently combined. In such cases the usual method is to scour the tussah in a soap lather, as already described in Chapter I, in presence of sodium perborate as bleaching agent; followed by alternating treatment with hydrogen peroxide and blankite (Badische). The slightly yellow tinge still remaining on tussah bleached with hydrogen peroxide or sodium peroxide can also be removed by the same alternating treatment.

Permanganate of potash can also be used for tussah when full bleach is not required; but the results are less satisfactory than with hydrogen peroxide. The tussah is entered in a bath of 5 % of permanganate and warmed slowly to 50° C. The silk, which is stained brown by the reduced manganese perhydroxide, is then treated in a sulphurous acid bath, prepared with bisulphite and the corresponding quantity of hydrochloric acid. Permanganate does not bleach tussah beyond the cream stage; and if white is required, the silk must be further bleached with hydrogen peroxide. Cream, however, is quite suitable as a ground for dyeing many shades, a full white being only required for a few delicate colours. The original colour of the tussah is generally lightened considerably by the removal of the brown colouring matter in the scouring process. The difference in the reports on the behaviour of tussah silk may be explained by the number of wild silks met with in commerce under this name, the author having frequently had specimens which scoured perfectly with Marseilles soap after a preliminary damping in soda solution, without exhibiting any stickiness of the fibre. A tussah of this character after being treated in two soap baths was cream in colour, the soap baths being blackish-brown, and the silk could be dyed without bleaching, or at any rate a single medium bleach with hydrogen peroxide would suffice.

Loading Tussah.—The loss of weight sustained in scouring varies up to 30% according to quality, and to make good this loss the silk is loaded. Since the fibre serves merely as a substratum for the loading agents, the methods employed for loading true silk are also applicable to tussah. In general, however, the loading is not carried to anything like the same extent; for one reason because the tussah filament is already thicker and plumper. Moreover, the fibre is less suitable for loading, owing to the absence of the bast which is the real carrier of the loading agents; whilst the so-called "bast" of tussah is too hard, and ill adapted for taking up large quantities of these materials. Consequently, the excessive loadings applicable to true silk would be difficult to obtain on tussah. According to the statements of some authors, tussah is better able to withstand the destructive influence of loading with tin and iron. Never having practised loading on tussah, the author cannot speak of the matter from personal experience, but he has no great belief in this alleged resistance to tin and iron.

Dyeing Tussah

It is generally stated in the literature that the affinity of tussah for dyestuffs is inferior to that of true silk; but the author, who has dyed a great deal of tussah, cannot confirm this. According to his experience, tussah has a greater, and even considerably greater, affinity than mulberry silk for dyestuffs. In his demonstration experiments for students he has repeatedly used tussah to show the rapid absorption of dyes, employing warm solutions of basic acid and substantive dyestuffs, and immersing the scoured tussah, from the second bath, directly in the dye-bath, without previous rinsing. Baths containing 2–3 % of dyestuff (based on the weight of the tussah) became water-white in one to two seconds.

The absorption proceeded with such rapidity that the whole of the dyestuff was taken up immediately by the lower portion of the hank in the bath, so that none remained to colour the upper portion. Some basic dyestuffs, *e. g.* nigramine, draw completely, in the cold, on to tussah that has been put through the three soap baths. This high affinity for dyestuffs explains the great difficulty, mentioned by all the authorities, in getting tussah to dye evenly—which cannot be reconciled by their other assertion that the affinity for dyestuffs is slight. Consequently, if the use of bast soap is recommended in dyeing tussah, there is nothing to urge against it; but it is doubtful whether the tussah dyer will always have bast soap available, because it is necessary to use bast soap from true silk, and not the dark brown baths resulting from the scouring of tussah. In case of need, however, the bast soap obtained in scouring chappe silk may be used. Nevertheless, the use of bast soap is by no means essential, Marseilles soap giving equally good results. With basic and substantive dyestuffs, a slight addition of acetic acid is an advantage, sulphuric acid being used with acid dyestuffs; but in the case of substantive and acid dyestuffs, it is advisable to add the acid by degrees, and not all together at the start. The author also considers it preferable not to raise the temperature so quickly to boiling, since, in his experience, boiling is unnecessary and even harmful. Tussah is not a homogeneous filament like true silk, but consists of a bundle of fibrils which are dissociated into their elements by prolonged boiling. Tussah frills out in boiling, and the extremely delicate, fine fibrils easily felt together to such an extent that this cannot be rectified by any amount of stretching on the wringing-post. This circumstance that tussah consists of a number of delicate fibrils also affords a direct explanation of the rapid absorption of the dyestuffs by capillarity, in comparison with true silk which is a compact, homogeneous filament into which the dye must penetrate from the outside, and therefore takes longer. For the above reasons, the author always works at temperatures below boiling-point when dyeing tussah, preferably at 75–80° C.; and, given a gradual raising of the bath temperature and careful addition of the acid, has never had to complain of uneven dyeing. Steinbeck is even more cautious, and recommends a bast-soap bath soured with sulphuric acid until the reaction is neutral. The author, however, cannot agree to his proposal that the bath should be boiled up repeatedly during the dyeing process. The same applies to Silbermann's statement that bleached tussah tends to give variegated dyeings in light shades because it contains oxidation products of the natural colouring matter, this substance being removed, without oxidation, by three soap baths, with a little carbonate of soda added in some cases. On the other hand, he agrees that the vitreous lustre of tussah makes the production of dark shades difficult; but he has never found that hot soaping strongly attacks bleached tussah.

Moreover, this would not harmonise with the unanimous opinion that tussah is less sensitive to alkalis than true silk; and since this latter is not injured by boiling-hot soap baths, there is no reason to suppose that the less sensitive tussah would be either.

All dyestuffs that are suitable for silk can be applied to a properly scoured, and if necessary, bleached, tussah.

Basic dyestuffs are distinguished by a special affinity for tussah. They are best dyed in a bath of fatty soap, soured with a little acetic acid, the tussah being entered cold, and the bath warmed slowly. The dyestuffs draw even at a medium temperature. This class of dyestuff is particularly suitable for all light, delicate shades.

Acid dyestuffs are applied in a soap bath soured with a little sulphuric acid. With such of them as distribute with difficulty, the soap bath is indispensable; but those which distribute well may be dyed in water, soured with a little sulphuric acid, without fear of uneven dyeing.

Substantive dyestuffs all exhibit a great affinity for tussah. They are applied in the same way as the basic dyestuffs, soap being used with those that tend to dye unequally, but otherwise omitted. The dyeing temperature need not exceed 60–75° C. The method that is sometimes recommended, of dyeing with an addition of Glauber salt or common salt, or of soda and soap, is suitable, but is seldom used in practice.

Mordant dyestuffs have not hitherto been used for dyeing tussah, so far as the author is aware. Sulphur and vat dyestuffs, too, do not seem to have been used for tussah, although, owing to the great resistance offered by tussah to the action of alkalis, there is nothing to prevent their employment.

Tussah is dyed black and loaded in the same way as true silk. For example, the tussah is bottomed with 60% of fustic, 20% of ferrous sulphate and 5% of copper sulphate, and then hung, to oxidise in the air, after which it is washed, and dyed with 300% of logwood and 40%

of soap below boiling heat. If cutch is used for bottoming, the best temperature is 60–70° C.

Of late, black azo dyestuffs, that dye in an acid bath, have also been used, but the black lacks fulness. Brightening after dyeing is effected in the same way as for true silk; and the same applies to stretching and lustring.

CHAPTER III

WOOL-SILK

Wool-Silk and its Treatment before Dyeing

In order to produce a cheaper class of silk fabrics, silk is frequently woven in conjunction with wool. This practice ensures two advantages simultaneously, since it enables grège (unscoured raw silk) to be utilised, and all the subsequent treatments for improving the silk can be effected in the piece, *i. e.* the difficult manipulation of hank silk by hand can be replaced by machine work. On the other hand, there are certain drawbacks, the boiling soap baths requisite for scouring the grège having a bad effect on the accompanying wool, which begins to soften and swell up, and acquires a gelatinous character so long as the boiling temperature is maintained, the fibres sticking together, *i. e.* felting. Since this felting property, so desirable in the production of woollen fabrics, does more harm than good in wool-silk fabrics, worsted yarn (more or less completely bleached), which has a smaller tendency to felt or shrink, is used for weaving with grège.

The circumstance that wool-silk has always to be treated in the piece necessitates certain mechanical treatments, as a preliminary to dyeing, that may be regarded as a preparatory finishing process. The subsequent results of dyeing depend on the proper treatment of the wool-silk in this intermediate stage, which is therefore of greater importance than the actual dyeing. The various operations in this stage are gassing, crabbing, steaming, scouring, and bleaching; but they are not always taken in the same order, steaming, for instance, being not infrequently performed after scouring.

Gassing is a purely mechanical operation, the purpose of which is to remove the projecting tips of the fibres from the surface of the fabric by burning them off with a gas flame. The work is performed in a gassing machine, particulars of which can be found in any standard work on finishing.

Crabbing is also a mechanical process, consisting in treating the wool-silk fabric in boiling water under pressure, the object being to produce a mechanical and chemical change in the wool so as to reduce its tendency to shrink. At the same time, the shape of the fibres and their position in the fabric are stabilised, so that they will not be altered by the subsequent treatments. The work is always performed in a crabbing machine, the description of which also is outside the scope of the present work. The machine usually consists of three troughs, with the requisite winding, squeezing and guide rollers and means for keeping the fabric wide open. In crabbing, the fabric is wound tightly and smoothly on the lower roller, which revolves in boiling water. This treatment is repeated in the second trough, after the fabric has remained for some time in the hot water of the first; whilst, in the third trough, it is passed slowly through cold water to cool it down. The effect of the hot water on the tightly-wound fabric is to stretch the individual threads, and cause them to lie parallel, so that they can no longer twist or shrink, the subsequent cooling fixing the fibres in place. Repeated crabbing also improves the lustre. The degree of pressure applied, if any, depends on the quality of the goods, pressure making them feel hard, and also producing a watered effect. In the case of goods which are desired to remain soft, and such as tend to exhibit a watered appearance in consequence of the type of weave employed, the application of pressure is less advisable.

Steaming is intended to loosen the threads that have been more or less flattened by crabbing, and make them more accessible to the subsequent operation of scouring. For this purpose the goods are wound, smoothly and free from wrinkles, on perforated and domed hollow iron cylinders, then covered over with packing cloth or jute, dry steam being forced through the material from a steam pipe. The operation and apparatus are very similar to those employed in steaming woollens. Care must be taken to see that the steam is quite dry; otherwise the fatal "water stains" are liable to appear; and the steam must not be admitted at an excessive pressure. After steaming, the goods are preferably unwound and steamed again, being, for this treatment, wound so that the end previously outside is now in the middle, this ensuring uniform treatment. When the operation is over, the goods are left on the roller for some time, until thoroughly cool.

Wool-silks made with woollen yarn are sometimes met with, and these require somewhat different preparatory treatment. Light fabrics are subjected to a longer washing with fatty soap, and if the wool becomes slightly felted, raising and shearing may be necessary in cases, such as poplins, where a felted surface is not desired. Heavy fabrics are lightly milled with a milling soap low in soda, and preferably in a cylinder machine, the soap being removed by careful washing and the fabric then dried. Lustre fabrics are steamed, with more or less pressure, after washing.

Scouring or boiling-off is effected in the same way as for hank silk, *i. e.* in boiling-hot soap baths. Great care is, however, necessary, wool being very sensitive to the effects of such baths, becoming softer, whilst the fabric tends to develop folds, which the dyer has reason to dread. This result can be minimised by using weak soap baths, omitting alkaline soaps, shortening the boiling stage and restricting the handling of the fabric. The boiling-off should be conducted with soft, preferably condensed, water. The operation is conducted in a series of vessels, the fabric being led, wide open, through the machine. Any folds that may form should be removed by careful stenting and brushing over with soft brushes. Actual boiling should be avoided, a temperature of 80° C. being sufficient. After the operation is finished, the fabric is rinsed with warm water, and then with cold. Instead of soap, which is not an ideal method, Steinbeck recommends scouring with hydrochloric acid and sodium phosphate, though, even here, soap cannot be dispensed with entirely. The scouring is performed in jiggers, the first containing 3 parts of hydrochloric acid per 1000 of water, and in this the fabric is entered at 60° C., the goods being kept moving while the temperature is raised to boiling, whereupon 6 parts of sodium phosphate are added and the treatment continued for another two to three hours. The second stage consists of a weak soap bath, followed by rinsing. Loosely woven wool-silk fabrics can also be scoured with steam, being first treated in the jigger with a 5% solution of soap for one-half to three-quarters of an hour at 60–70° C., after which they are wound on a jacketed steaming cylinder and steamed. The steam passes centripetally through the fabric and removes the bast soap, which can be collected at the steam outlet valve of the cylinder. When (after one to two hours) any more bast soap ceases to come off, the steaming is continued for a short time, and the fabric is brightened with 2% of acetic acid, introduced through a funnel at the side of the apparatus and dispersed by the steam. The fabric can be partially dried by admitting warm air into the steaming cylinder. Wool-silk scoured in this way is ready for dyeing. The method, however, is only applicable to loose fabrics, such as poplins, bengalines and the like, but not for closely woven stuffs, such as gloria.

In all cases the scouring should be followed by a short steaming, except when steam is used for scouring.

Bleaching Wool-Silk.—Both silk and wool being animal fibres which can be bleached with the same agents and by the same methods, those described in an earlier section may be referred to. In practice, both sulphur, sulphurous acid and peroxide bleachings are employed, the fabric being dipped intermittently into the kier. Any soap present in the material must be carefully eliminated previous to bleaching; and, in view of the sensitive character of wool-silk fabrics, excessive bleaching temperature (boiling especially) must be avoided, as also over-long bleaching and an excess of free alkali, as they spoil the appearance and strength of the fabric. It is also necessary that the material should not be plunged too violently into the bleach liquor, or, on the other hand, insufficiently immersed. A combination of sulphuring in the sulphur chamber with subsequent bleaching in a weak bath of hydrogen peroxide has been found satisfactory, the bleaching effect being excellent and the strength of the fabric fully retained. Steaming may also be advantageously combined with bleaching.

Properties of Wool-Silk and its Behaviour towards Dyestuffs.—Though the two animal fibres in the fabric behave alike in presence of certain agents they differ in respect of others, as has already been seen in the case of soap. In general it may be said that wool is more sensitive than silk towards alkalis, but less so towards acids. Metallic salts, especially the basic salts of the heavy metals, are dissociated by both fibres, the metallic hydroxide (or perhaps also a salt of still higher basicity) being absorbed, although at different temperatures. Silk decomposes many of the basic salt solutions in question in the cold or at a moderate temperature, whereas greater heat is required to produce the same effect in the case of wool, prolonged boiling being sometimes necessary. All these differences, however, are insignificant and have practically no adverse influence on the subsequent dyeing.

A greater disparity is observed in the behaviour of wool and silk towards dyestuffs, though this is not appreciable at the start. The high affinity of silk for dyestuffs is well known, that of wool being not nearly so great; but it is in connection with the temperatures at which absorption takes place that the great difference arises, silk absorbing the dyestuffs as a rule between 60 and 80° C., or even lower, whereas wool requires 90–100° C., and sometimes prolonged boiling. This fact is explained by the chemical character of wool, the main constituent of which, keratin (which is also the chief substance in hair, nails, hoofs and horns), is a nitrogenous body which is not very active, chemically, at ordinary temperature, and does not become so until softened to the condition of a gel, at higher temperatures, at which wool takes up dyestuffs as readily, and in some cases to the same extent, as silk. Apart from the question of temperature, therefore, there is no appreciable difference between the two fibres in this respect, since all dyestuffs that will dye wool dye silk as well. This applies, however, only so long as a given dyestuff is used on the fibres separately, the case being different as soon as a dyestuff is presented to them simultaneously (as in the case of wool-silk fabrics) and is, as it were, compelled to choose between them. It is seldom that the election results in favour of either exclusively, and in many cases the difference in affinity is so small that the dyestuff may be said to have an equal affinity for both silk and wool. In others, however, a more decisive selective faculty is exercised in favour of either the wool or the silk, though both fibres are always dyed simultaneously. Only in rare instances is the difference so great that a dyestuff will dye, say, the silk, leaving the wool nearly or quite white (this is the case, *e. g.*, with rhodamine and new Victoria blue), or that the wool is dyed and the silk left untouched, as with naphthol yellow S, alizarine saphirol, indigocarmine, fast yellow and azofuchsine G. On the other hand, a given dyestuff will often dye the two fibres in different shades: for instance orange II. This difference in affinity is, however, by no means invariable, being dependent on and changing with the temperature. A dyestuff which has but little affinity for wool at 70° C. may exhibit great affinity for it at boiling heat; whilst one that will scarcely dye silk at all at 100° C., may do so strongly when the bath cools down to 60° C. The affinity can therefore be influenced by regulating the temperature, thus enabling a dyestuff to draw, at will, more to the silk or to the wool; and sometimes even, by prolonged boiling, to confine it to the wool exclusively. Since all dyestuffs can be applied to silk, the choice for those to be used on wool-silk is exercised in favour of such as are well adapted for wool.

Basing on the chemical constitution of the dyestuffs, it may be assumed that a strongly acid dyestuff will have a greater affinity for wool, whereas those of a more pronounced basic character, such as rhodamine, will tend to draw better on silk; and those in which the acid and basic groups are more equally balanced will dye both fibres approximately the same.

Finally, it may be mentioned that the divergent behaviour of a dyestuff towards the two fibres in question can be modified by the relative proportion of the two fibres in the fabric. Thus, it may easily happen that a given dyestuff will behave quite differently towards a fabric consisting mainly of wool, with the silk as merely fancy threads—such as small stars, flowers or stripes—than it will towards a wool-silk in which silk predominates.

Dyeing Wool-Silk

The bast soap that is almost indispensable to the silk-dyer must be discarded in this case, as it would make the wool too soft and the cloth flabby. On the other hand, Glauber salt is avoided, as far as possible, because it makes the silk rough and brittle in the event of prolonged boiling. Soft water is essential, hard water being softened beforehand; and the boiling must not be continued too long. The usual bath ratio is 1 : 25–30.

Self colours are always dyed in a single bath, a second being only used for shading the silk; and, given a little practice, there is no difficulty in dyeing both silk and wool to the same shade, by suitably regulating the temperature and, if necessary, adding a suitable amount of dyestuff to the bath. As a rule, the wool is dyed rather deeper than the silk, as this improves the appearance of the fabric.

Basic Dyestuffs.—These find only restricted application, chiefly for shading. If used alone, they are dyed in a neutral liquor, or with a slight addition of acetic acid, at about 80° C., higher temperatures giving weaker dyeings.

Most of the basic dyestuffs act more powerfully on the silk than on the wool; and some of them, when used in a cold acetic bath, dye silk preferentially, but the wool only slightly, *e. g.* safranine, brilliant green and methylene blue.

Acid Dyestuffs.—This is the class of dyestuffs mostly used for wool-silk. If the fabric chiefly consists of wool, it is dyed in presence of 5–10% of Glauber salt and 1½–3% of sulphuric acid, at about 90° C. At lower temperatures and with more acid the dyestuff draws chiefly into the silk; whilst at higher temperatures, and especially at boiling heat, the wool is dyed most. Alkali blue, on the other hand, is dyed with 10 % of borax, for an hour at 80–90° C., followed by washing and souring. If silk predominates in the fabric, it is better to leave out the Glauber salt, using sulphuric acid only; or, according to Steinbeck, with an addition of 10 parts of sulphate of magnesia per 1000 of bath liquor.

Since strongly acid baths are as little used as alkaline in dyeing wool-silk, it is occasionally the practice to add 2–4 % of cream of tartar, and boil up the liquor for a short time before putting in the dyestuff. In this way the cream of tartar is completely absorbed by the wool. The bath is then cooled and a double quantity of sodium phosphate is added, this being almost entirely taken up by the silk. The actual dyeing is then begun. This method is specially applicable when using dyestuffs (such as induline and nigrosine) that have a stronger affinity for silk than for wool; and in this case an addition of ammonium acetate is also very useful.

The requirement that the wool should be dyed rather darker than the silk can, as already mentioned, be met by regulating the temperature; and the same result can be obtained by increasing the amount of acid in the bath;

high acidity should be avoided as much as possible, and on no account be employed for light shades. As an illustration of the manifold application of acid dyestuffs on wool-silk it may be mentioned that the silk can be dyed with these dyestuffs in the cold; consequently, if the silk alone is to be dyed and the wool left white, all that is necessary is to use a cold bath. If the main object is to dye the wool, the bath must be boiled for a short time, and between these two extremes a whole series of gradations can be obtained, either the silk or the wool being the more strongly dyed, or equally. Should the silk come out too pale, it can easily be topped with basic dyestuffs, in which case, after the acid bath is exhausted and has cooled down to about 70–80° C., the requisite amount of dissolved basic dyestuff is added, and the fabric treated for another quarter of an hour without steam, and finally rinsed.

By virtue of the divergent absorptive capacity of the two fibres at different temperatures, it is quite a good plan not to add the whole of the dyestuff to the bath at once, but first to dye the wool to shade or pattern with a portion of the dyestuff, at nearly boiling heat, then cool and, if necessary, add sufficient dyestuff to dye the silk. The whole art of dyeing wool-silk in an acid bath consists in maintaining the proper temperatures and in the compounding of the dye-baths, taking into consideration the concentration and the amount of acid to be used.

Most of the acid dyestuffs dye both wool and silk to the same extent, or nearly so; but a whole series—*e. g.* acid fuchsine, the eosines, orange II, fast yellow, naphthol yellow S, tartrazine, wool green, alizarinecyanine green, alizarine saphirol, Victoria violet, naphthylamine black, etc.—have less affinity for silk. A smaller number, when used in a briskly boiling bath of low concentration and with an addition of 15–20 % of acetic acid, will not dye the silk at all; for example, the azofuchsines, fast yellow, naphthol yellow, the tartrazines, alizarine emeraldol, alizarine saphirol B, Victoria violet, etc. On the other hand, a few (*e. g.* croceine scarlet 8B, brilliant acid green 6B, wool blue N extra, brilliant wool blue, the acid violets, etc.) draw mainly on the silk and but little on the wool if used in a cold bath along with 5% of acetic acid.

The Substantive Dyestuffs are also well adapted for dyeing wool-silk, and are used because many of them give extremely fast colours. They must be employed in either a neutral or slightly acid bath, the choice depending on the fastness of the dyestuff to acid. The most sensitive in this respect, such as Congo, benzopurpurine, etc., require a neutral bath, that is to say in water alone, without any Glauber salt, though a small quantity of this, or of ammonium acetate, may be added towards the end. One may also dye direct with 5–20 % of Glauber salt, entering at about 60° C. and raising the bath to the boil. The more acid-resisting dyestuffs are dyed in a weakly acetic bath, Glauber salt and ammonium acetate being added near the end, if required. The acetate gives a somewhat darker shade to the wool; or the dyeing may be performed as above and 1–2 % of acetic acid added after the goods have been boiling ten to twenty minutes. If the wool is not then properly covered, the boiling is continued; and the silk is dyed afterwards, when the bath has cooled down to 60° C., with an additional amount of dye if necessary. If either the wool or the silk is then not dark enough or true to shade, the operation is continued at boiling heat, with more dyestuff when necessary. The colours obtained with substantive dyestuffs are distinguished by fastness to alkali and washing, but are not bright enough for some purposes, in which contingency they may be topped with basic dyestuffs, this having but little adverse effect on their fastness to milling, though their fastness to light is impaired. The substantive dyestuffs which dye in an acid bath can also very well be combined with acid dyestuffs in one bath, though this lessens the fastness of the substantive dyeings to milling.

Most substantive dyestuffs dye silk and wool equally, or nearly so. A few, such as benzo red 10B, chloramine yellow, thiazol yellow, benzo green, brilliant azurine 5G, benzo violet, etc., act more powerfully on the silk; whilst others—*e. g.* Congo rubine, geranine G, benzo blue 2B and heliotrope BB—dye the wool most.

Sulphone Dyestuffs are dyed in the same way as the substantive dyestuffs.

Mordant Dyestuffs are seldom used, because the mordanting of the two fibres concurrently leads to irregularities. The mordants used are chrome, alumina, iron or tin, the corresponding basic salts (basic chromium chloride, basic sulphate of alumina, basic ferric sulphate), being employed, the tin mordant consisting of tin salt in combination with cream of tartar. It is best to mordant cold, though this entails the risk of the wool being insufficiently mordanted and not taking up enough dye afterwards. If heat is employed, the basic salts should not be used, being replaced by the normal salts and a corresponding quantity of cream of tartar, and the bath raised to near boiling point. Under these conditions the wool is mordanted to a greater degree than the silk.

In the former case the wool will dye too pale, and in the latter too dark; and in any event it is difficult to get uniform dyeings. This is the reason why mordant dyestuffs are comparatively seldom used, and why they are only resorted to when the colours are desired to be faster to washing and soap than is attainable with substantive dyestuffs. Gloria umbrella fabrics, in particular, are preferably dyed with mordant dyestuffs, both dye-woods and alizarine dyes being used. The dyeing is performed either in a bast-soap bath, or in water acidified with sulphuric acid (no bast soap); or, again, in a bast-soap bath soured with acetic acid. In order to obtain more uniform distribution, the mordant dyestuffs are frequently dissolved in ammonia, the solution being added to the bath in small quantities at a time. The dyeing process is carried on in the same way as for wool, the temperature being raised gradually and boiling continued for one to one and a half hours.

Mordant Dyestuffs can, of course, also be dyed by the acid single-bath method for unmordanted wool, and after-chromed in the same bath.

Dichroic Effects on Wool-Silk

It has just been seen that one group of acid dyestuffs dyes wool at boiling heat more strongly than silk, and that, with prolonged boiling, the whole of the dye sometimes goes into the wool, leaving the silk white. This extreme differentiation, however, is not obtained direct merely by dyeing, because the silk also is coloured, though to a smaller extent, and only comes out perfectly white after the dyed wool-silk has been put through a bran bath. The effect of this bath can be intensified by a little soap or ammonia, or by afterwards keeping the fabric for a quarter to half an hour in a bath of warm water containing a little soap or ammonia. This method enables dichroic effects to be obtained, and that, too, in the simplest form: wool dyed, silk white.

According to the type of weave of the wool-silk fabric, the white silk shows up as a design, or is so intimately interwoven with the wool that—as a result of the reflection of the light—first one colour and then the other seems to predominate, thus producing what is known as "shot" colouring. The acid dyestuffs suitable for this purpose comprise, *inter alia,* indigocarmine, picric acid, naphthol yellow S, tartrazine, azofuchsine, Victoria violet 4BS, azo-Bordeaux, fast yellow extra, the Höchst chromotropes, alizarine saphirol, naphthol green, acid fuchsine, crystal ponceau, red violet 5RS, amaranth, cochineal red, orange GG, quinoline yellow, and acid green. Since it is thus possible to obtain dyeings in which the silk is left untouched, it cannot be difficult to get dyeings in a variety of colours by afterwards using dyestuffs which will draw exclusively on to the silk without dirtying the wool. For this purpose, basic dyestuffs are usually selected that have a preference for silk, or acid dyestuffs with the same property, such as methyl blue for silk, silk blue, the eosines, indulines and nigrosines, and the whole of the substantive dyestuffs. The basic dyestuffs are used in a cold, neutral, water bath, the acid and substantive dyestuffs in a warm bath (40–50° C.) with a little acetic acid. The process thus becomes of the two-bath type, the wool being dyed first. In order to minimise the staining of the silk, a fairly concentrated bath is used, containing 20 % of acetic acid, and the operation is conducted quickly, by boiling for about a quarter of an hour. The silk also being slightly coloured, the fabric is put through a bran or soap bath at 40° C., which clears the silk completely. This fibre is then dyed quickly in a fresh, cold bath, also fairly concentrated, so as to prevent the wool from absorbing dye. The higher the bath temperature, the larger the amount of dye taken up by the wool. To retard this absorption in the case of basic dyestuffs, a little soap is added to the bath. A similar dichroic effect is obtained by dyeing the wool with 6–10 % of naphthol black B in an acetic acid bath at boiling heat, and then stripping the black from the silk in a boiling bath of ammonium acetate, which leaves the silk perfectly white and ready for dyeing at once with basic dyestuffs.

Another plan is to top the silk with acid dyestuffs in a cold bath, in which case acetic acid is added in dyeing. To obtain black wool dyeings with coloured silk effects, use is made of chromotropes and similar dyestuffs, such as azofuchsine G and B or azo Bordeaux, the wool being dyed with 5–8 % of these, at boiling temperature, with addition of 20 % of acetic acid, then oxidised in the same bath with 3 % of chromate of potash, the silk being next stripped in the bran bath. In the same way the silk may be topped with substantive dyestuffs, in a cold bath containing acetic acid. The following examples may serve as illustration of the principles.

Shot Effects in Two Baths.—(1) Wool: azocochineal, Indian yellow; silk: brilliant green. (2) Wool: azocochineal; silk: turquoise blue. (3) Wool: azofuchsine G., chromed; silk: new Victoria blue B. (4) Wool: azofuchsine G, chromed; silk: Indian yellow G.

Shot Effects in a Single Bath.—(1) Wool: fast yellow extra; silk: rhodamine B. (2) Wool: naphthol yellow S; silk: methylene blue. (3) Wool: Victoria violet 4BS; silk: auramine. (4) Wool: alizarine saphirol B; silk: safranine. (5) Wool: cochineal scarlet PS; silk: brilliant green. (6) Wool: fast red NS; silk: turquoise blue BB.

Finally, two-colour effects in a single bath can be obtained by using suitable combinations of dyestuffs which preferentially dye silk with such as select wool, in the one bath. In the first stage, 10–20 % of acetic acid and the necessary acid and basic dyestuffs are added, the wool-silk is entered at 30–40° C., the bath being slowly raised to boiling heat and boiled until the wool is sufficiently dyed. In the second stage, the steam is shut off and the dyestuff allowed to draw on to the silk, shading being afterwards effected with basic dyestuffs at below boiling heat.

CHAPTER IV

HALF-SILK FABRICS

HALF-SILK FABRICS AND THEIR PREPARATORY TREATMENT

HALF-SILK fabrics are composed of silk and cotton, and the goods are therefore dyed in the piece. The fabric as it comes from the loom is not in a proper condition for dyeing, but, as in the case of wool-silk, must be put through a series of preparatory treatments, partly of a mechanical and partly of a technical character. The treatment is, however, simpler, and is restricted to gassing, boiling-off and bleaching.

Gassing is performed in the same way as for wool-silk, in the gassing machine, and this treatment may be regarded as known.

Boiling-off, or scouring to free the grège from sericin, also removes oil and size. It is performed in a boiling bath of fatty soap, white soap being generally used for light coloured fabrics, and green Marseilles soap for dark. Low-grade fabrics containing much cotton, such as cheap umbrella stuffs, are boiled-off with an addition of olive oil soft soap. The usual quantity of soap is 10 parts per 1000 of bath liquor. The bath should be set with soft or softened water, preferably condensed water, in order to guard against the formation of lime stains caused by precipitated lime soaps. In many cases the addition of monopol soap does good service in the bath, this class of soap having the valuable property of forming soluble compounds with the salts of lime and magnesia in the water, and thus preventing the precipitation of lime and magnesia soaps. The usual addition is 2–4 parts per 1000 of liquor. Marseilles soap is added in a predissolved condition, the bath being then boiled up, the steam turned off, and the goods entered and boiled for about two hours. The boiling temperature must be maintained throughout, but violent ebullition is injurious to the silk and must therefore be avoided. Fabrics that are to be left white, or dyed in light shades, must be put through a second soap bath, of half strength, in which they are treated for an hour. This is usually followed by a weak soda bath, at hand temperature, and one or two cold rinsing baths, the operation being completed by a weak bath of hydrochloric acid (to extract the final traces of lime) and a final rinsing in cold water.

The baths are not usually renewed for each parcel of fabric, the old baths being employed as much as possible and replenished by adding $\frac{1}{2}$–$\frac{1}{3}$ the original quantity of soap. These baths cannot be used as "bast soap," since, in addition to sericin, they contain the oil, size and any impurities present in the cotton. As a rule, they cannot be replenished more than 3 times, as they would then be too dirty. The second boiling-off must always be performed in a fresh soap bath, which can then be used as the first bath for the next parcel. In large works the scouring of half-silk fabrics is carried out in large boiling vessels, consisting of a combination of cast-iron jiggers with brass rollers, feed and delivery mechanism and intermediate squeezing rollers. The fabric is boiled-off in the first and second vessels, and successively rinsed, soured and rinsed again in the others, the operation being thus continuous. The machines are driven by a small steam engine. The goods are passed slowly through the succession of vessels, to give the baths sufficient time to do their work. Any folds that may form are smoothed out with soft brushes; but this contingency seldom arises, the goods being kept on the stretch from start to finish.

Lighter fabrics are usually boiled-off in kiers, lined with packing cloth to protect the silk from rubbing. The fabric is either kept on the move all the time by means of hand reels, or else only reeled at the beginning and end of the process, being left submerged in the interval.

Half-silk plush fabrics are boiled-off with the aid of star frames similar to those used in vat dyeing, though they may also be treated in the kier by means of hand reels. Ribbons are boiled off in the same way as yarn, being afterwards drained in the hydro-extractor, and either bleached, dyed or dried.

Some umbrella fabrics are crabbed, steamed and singed again after boiling-off, in the same way as wool-silk (*q. v.*).

Bleaching follows directly on the boiling-off process, but is only needed for pale, delicate colours; and is superfluous when, as is often the case, the fabric is woven from bleached cotton yarn. The bleaching agents now used are hydrogen peroxide and sodium peroxide, the others being unsuitable. Sulphuring only bleaches the silk; bleaching powder and Eau de Javelle are too alkaline and corrode the silk. The bleaching baths are prepared and used in the manner already described.

PROPERTIES OF HALF-SILK AND ITS BEHAVIOUR TOWARDS DYESTUFFS

The two textile fibres contained in half-silk fabrics differ very extensively in their behaviour towards most reagents, and in some cases are diametrically opposite in this respect. For our purposes there is no need to go into this question as regards reagents in general, but we must take into consideration this behaviour so far as it relates to acids, alkalis, chlorine, metallic salts, tanning agents and dyestuffs, because a knowledge of this is indispensable for understanding the process of dyeing half-silks.

Silk, being an animal fibre, is insensitive towards dilute mineral acids, such as sulphuric and hydrochloric acids, even at high temperatures, for silk may be boiled in dilute sulphuric acid baths without being appreciably corroded. Concentrated warm sulphuric acid dissolves the fibre to a brown syrup which dissolves to a clear solution in water. Boiling hydrochloric acid dissolves silk rapidly and completely, but the dilute acid has very little effect.

Cotton is a vegetable fibre, and as such is little affected by cold and dilute acids; but, on the other hand, hot dilute mineral acids, as soon as a certain concentration (which is different for each acid) is attained, make the fibre friable and reduce it to the state of a white, yellowish or grey powder. This destructive action also occurs when the dilute acid is concentrated on the fibre, as the result of the evaporation of the water, as is the case in the carbonising process. In concentrated sulphuric acid, cotton swells up at first, and is then transformed into a gelatinous mass, which dissolves completely, with formation of dextrin if the action is prolonged.

Sulphurous acid, preferably in the form of vapour, bleaches silk, but not cotton.

Strong nitric acid destroys silk rapidly and completely; whilst dilute nitric acid, which contains nitrous acid, imparts a yellow stain that is fairly fast to light and completely so to washing, xanthoproteinic acid being formed. Cotton, when boiled with concentrated nitric acid, is oxidised, with formation of oxalic acid and other products, but no yellow coloration results. Cold concentrated nitric acid (preferably in presence of a little sulphuric acid) transforms cotton into the various nitrocelluloses, of which gun-cotton and collodion (a solution of dinitrocellulose in ether-alcohol) are the best known, collodion being the material from which artificial silk is manufactured.

Anhydrous acetic acid dissolves silk readily and completely at higher temperatures, but the dilute acid has no action. At high temperature and under pressure, the anhydrous acid reacts on cotton to form acetyl cellulose, the so-called acetate silk.

Alkalis dissolve silk rapidly and completely in the warm; but even concentrated solutions have practically no action at 0° C. Dilute alkalis merely cause the silk to swell, with partial solution. Ammonia has no appreciable effect, even when heated. Cotton swells up strongly in solutions of the caustic alkalis, and becomes translucent, without dissolving, but shrinks and becomes thicker and shorter. The fibre treated in this manner retains its new properties, even after being washed in water, and exhibits an increased affinity for dyestuffs. This behaviour is the basis of the mercerising process. Cotton thus treated and then stretched again to its original length, acquires a silky lustre.

Alkali carbonates have less effect than alkalis on silk, and they do not shrink cotton.

Chlorine and the soluble hypochlorites destroy silk easily and quickly. The alternate action of hypochlorite solution and atmospheric air containing carbon dioxide does not destroy the fibre, but improves its absorptive capacity for dyestuffs. No bleaching effect is produced. Cotton is entirely destroyed by chlorine, soluble hypochlorites having a less energetic action. Weaker solutions destroy the natural yellow colouring matter of cotton in the cold, without appreciably affecting the fibre, which, however, is more or less attacked and partially oxidised on prolonged exposure or in presence of stronger solutions.

Certain metallic salts are wholly or partially decomposed by silk, as has already been seen in connection with mordants. This dissociative power is only possessed to such a slight extent by cotton that actual mordanting in the case of cotton is confined, in practice, to alumina salts.

Tannins are taken up by silk from their solutions, to the extent of 15–20 % of the weight of the silk, at 80–90° C., the silk increasing in volume and retaining the absorbed tannin tenaciously. Strangely enough, this absorption of tannin decreases the capacity of silk for taking up basic dyestuffs, and may reduce it to almost nil. Cotton, on the other hand, has no affinity for tannins, and although it will take up a small quantity, in the cold, parts with it again when rinsed with warm water. In order to fix tannin on cotton, subsequent rinsing must be omitted. Instead of merely drying the cotton and thus securing a certain amount of tannin on the fibre, the tannin is usually fixed by a treatment with tartar emetic. Cotton mordanted with tannin in this way has a very great affinity for basic dyestuffs.

In addition to the foregoing, silk and cotton exhibit striking differences in their behaviour towards dyestuffs.

Basic Dyestuffs have a great affinity for silk, which they dye very strongly in a neutral bath or one slightly soured with acetic acid. The affinity of cotton, on the other hand, is very slight; so much so that many authors speak of cotton as inert to these dyestuffs. This, however, is inaccurate, for if cotton be treated with a hot basic fuchsine solution, the fibre appears to be strongly dyed; and although it is true that the greater part of this dye is extracted on rinsing with water, and still more on soaping, there still remains a certain amount of fuchsine in the fibre. True, it is only a dull pink, but one certainly cannot say that cotton is indifferent to fuchsine. The same kind of thing is observed when the experiment is repeated with chrysoidine or Bismarck brown; and still more so in the case of basic safranine azo-dyestuffs, such as indoine. The shades obtained by simple treatment in a bath of hot water cannot, however, be classed as dyeings; and if strong shades are required with basic dyestuffs, the cotton must be mordanted with tannin and tartar emetic.

Acid Dyestuffs dye silk in an acid bath, but not cotton; and though there are a few exceptions, they mostly require the cotton to be mordanted beforehand with sodium stannate and alum, or dyed with alum by the single-bath method. To these belong: croceine scarlets, orange II, quinoline yellow, brilliant acid green, alizarine saphirol, etc. The resulting dyeings, however, are of inferior value and are of no interest in connection with half-silk fabrics.

Substantive Dyestuffs dye silk in a bast-soap bath soured with acetic acid. On cotton they draw in a neutral Glauber salt bath, but the dyeings are much weaker than on silk.

Mordant Dyestuffs, as has been said, are seldom used for silk; and they are still less so for cotton, since, with the exception of alumina, there are no proper metallic mordants at present available for cotton. Consequently, these dyestuffs are of no interest in connection with half-silk.

Sulphur Dyes are not to every one's taste for dyeing silk; and so much the more excellent is the service they render in the dyeing of cotton.

Vat Dyestuffs dye both silk and cotton by the same method.

DYEING HALF-SILK

The logical conclusion to be deduced from the particulars just given is that the dyeing of half-silk is by no means a simple operation, especially in a single bath, because the methods of dyeing either of the two fibres are unsuitable for the other. If, on the other hand, one contemplates dyeing the silk and cotton independently, with the necessary consideration for the other fibre in each case, the process is theoretically simpler, but in practice a two-bath method. Formerly, when only acid and basic dyestuffs were available, it was essential to dye in two baths; but now this method is avoided as much as possible. In fact, at the present time, the basic and acid dyestuffs are of merely subordinate interest for dyeing half-silk, because they cannot be used in a single bath, and they are employed solely for shading single-bath dyeings.

The present practice is to use the substantive dyestuffs almost exclusively, as they are able to dye both silk and cotton in the same bath. The method employed for silk—bast-soap bath soured with sulphuric acid—is not, however, applicable, since the acid in the hot bath would attack the cotton. On the other hand, the usual bath of Glauber salt and soda, prescribed for substantive dyestuffs, is also inapplicable, as the soda would corrode the silk. Consequently, both the acid and the soda are omitted, and a neutral Glauber salt bath is used. Soft water is necessary, hard water being softened by boiling with a little soda. The usual bath ratio is 1:20, a weaker bath being taken for light shades, and a stronger one for dark shades. It is best to work with a closed steam coil, so as not to weaken the bath continuously. Light shades equalise better in a dilute bath than in a more concentrated one. Certain of the substantive dyestuffs do not distribute very evenly, and in such cases a slight addition of soap to the bath is beneficial; and many half-silk dyers always use Glauber salt and soap. According to the depth of shade desired, the proportions vary between 5, 10 to 20 % of Glauber salt and 1, 2 to 5 % of Marseilles soap. The bath is raised to boiling heat and the pre-dissolved dyestuff added, steam being then shut off, and the well-damped fabric entered and worked about at 90–95° C., according to the depth of shade: 60° for light shades, and intermediate temperatures for medium shades.

The additional soap serves another purpose, viz. to retard the absorption of dye by the silk and drive it more on to the cotton, so that the silk comes out the lighter of the two. In this respect, however, the substantive dyestuffs differ among themselves in any event, for whilst most of them dye silk and cotton equally, or nearly so, in a neutral Glauber salt bath, a second group dyes the cotton most, and a third the silk most, under the same conditions; and a fourth series produces different shades on the two fibres. By adding soap to the dye-bath the conditions are modified in favour of the cotton, in the sense that the cotton is rather more strongly dyed than the silk in all cases. In this respect, too, the substantive dyestuffs do not all behave alike, and, in certain circumstances, the affinity for silk is so slight that the silk is hardly dyed, if at all. For example, in a bath of 10 % of Glauber salt and 5 % of soap, chloramine orange G, chloramine yellow GG, direct yellow R, benzo pure blue, etc., leave the silk nearly white. Every fresh addition of alkali to the bath increases the affinity of the substantive dyestuffs for cotton, and lowers it for silk.

If the dye-bath be prepared with 10 % of soap and 5 % of soda, a large number of the substantive dyestuffs will dye the cotton only, leaving the silk perfectly or nearly white. The dyer has therefore a means of control which enables him to drive the dyestuff more or less on to the cotton and withhold it from the silk. This is undoubtedly interesting, but is of little practical importance, since the purpose of dyeing half-silk is to dye the silk and not to leave it white, except, of course, in cases where dichroic effects are desired.

In working with substantive dyestuffs, especially when soap is used, the dye-baths are not fully exhausted. In order to operate both rationally and economically—since soap makes the baths expensive—the old baths are used over again, so that the dyeing is performed in an old bath and the cost of continually preparing new baths is saved. This method is specially advisable for dark shades, in which case the baths are always only partly exhausted. In replenishing the old baths, the amount of dyestuff required is one-third to one-half that used in the first bath, and the only addition of Glauber salt and soap necessary is approximately that required to replace that carried away in the dyed fabric. In the case of soap, however, this applies only when soft water is used, since, with hard water, an allowance must be made for the soap removed by precipitation of lime soaps as well. On account of the gradual decomposition that sets in, it is not advisable to use old baths too long. As an alternative to use over again, the baths can, of course, be utilised in the preparation of lighter shades of the same or similar colours.

It must seem curious that no experiments have been made in the opposite direction, viz. to drive the dyestuff more on to the silk; but this result is easily attained by slightly souring the Glauber salt with acetic acid, this measure altering the conditions of affinity, and checking the tendency of these dyestuffs to draw on to the cotton and therefore allowing them to act more on the silk. This seems a more important consideration than checking their action on the silk, because most half-silk fabrics are woven in such a manner that the silk shows up on the face and the cotton on the back of the material. Consequently, the dyeing of the silk is the chief consideration, and that of the cotton a secondary matter, only the silk face being visible when the fabrics are made up. For the same reason, it is not so very important that the cotton should match the shade of the silk exactly in half-silks of this particular kind. If, on the other hand, the silk and cotton are uniformly interwoven, as is the case with cheap umbrella fabrics, for instance, or if the silk forms a pattern—stripes, dots, stars, flowers, etc.—full attention must be bestowed on the dyeing of the cotton, no matter whether the single or two-bath method is adopted.

If the desired shade is not obtained with substantive dyestuffs, shading is easily effected with basic dyestuffs, preferably in the same bath. The goods are entered into a cold or lukewarm bath slightly soured with acetic acid, the dyestuff drawing on to both silk and cotton and usually rather more strongly on to the former. It is perhaps not quite so well known that a few of the acid and faintly acid dyestuffs can be dyed in a bath of Glauber salt and soap, and can therefore be used for shading silk. Most of them, however, dye the cotton a little as well, but a small number, such as sulphone yellow 5G, alkali fast green 3B, brilliant acid green 6B, fast green CR, alizarine irisol and acid violet 6BN, leave the cotton untouched. Another method of shading the silk is with acid or faintly acid dyestuffs in a lukewarm bath with a little acetic acid. In this case, also, most of the dyestuffs dye the cotton to some extent, the best in this respect being alkali fast green 3B and 3G, the acid greens, alizarine pure blue, brilliant acid blue EG, FF and V, alizarine irisol, acid violet 4RS and fast wool violet B.

The Basic Dyestuffs are seldom used on half-silk; and when they are, the cotton must first be mordanted by entering the fabric (previously damped with warm water) in a cold bath of 2–4 % of tannin, and leaving it all night. The silk will not take up tannin from cold liquor. Next day, the fabric is entered, without rinsing, in a cold bath of 1–2 % of tartar emetic for half-an-hour, then well rinsed, and dyed in the cold (or with slight warming) with or without acetic acid. At lower temperatures the basic dyestuffs draw preferably on to the mordanted cotton, but more on to the silk at higher temperatures, so that, by suitably regulating the temperature, the dyer can obtain the same shade on both sides of the fabric.

Acid Dyestuffs can be used for dyeing the silk by the two-bath process, and also, as already mentioned, for shading the silk in half-silk fabrics dyed with substantive dyestuffs.

Diazo Dyes are used for dyeing half-silks, such as umbrella fabrics, that have to stand water. The dyeing is carried out in the same way as for substantive dyestuffs, the goods being then rinsed, diazotised and developed as in the case of whole silk, and finally well rinsed and soaped. If necessary, the silk can be shaded in a fresh bath by one or other of the methods already described; and as the diazotised dyes will generally stand topping, higher temperatures may be used in the shading baths. What has already been said, in connection with the substantive dyestuffs, as regards the use of old dye-baths, applies equally in the present case and also in respect of the diazotising and developing baths.

Sulphur Dyestuffs can be used on half-silk in a single bath, prepared and used in the same way as for silk (*q. v*). Since these dyestuffs draw chiefly on to the cotton at low temperatures, and on to the silk in the warm, the dyer is again in a position to obtain the same depth of colour on both sides by regulating the bath temperature accordingly. If necessary, the silk can be shaded, in a fresh bath, with acetic acid and acid dyestuffs.

Vat Dyestuffs give very fast dyeings on half-silk, and are used in the same way as for silk (*q. v.*)

In comparison with the above-described single-bath methods, the recipes for dyeing half-silk in two baths have lost interest; but, as they are still occasionally used, a few of them will now be given.

The silk is first dyed, as described above, with readily distributable dyestuffs, in a slightly acid bath, except that the bast soap and soap are better omitted on account of their unfavourable influence on the subsequent dyeing of the cotton with basic dyestuffs. After rinsing, the fabric is left all night in a tannin bath. It is advisable to keep the silk rather lighter than is finally desired, because it always takes up a little dye from the second bath. The tannin bath is preferably cold, as if warm it acts on the silk as well. Practical experience has shown an addition of hydrochloric acid to the tannin bath to be beneficial. On the following morning the fabric is entered in a bath of tartar emetic. Uniform mordanting with tannin is difficult to obtain with half-silk, and uneven colouring is very liable to occur. This will be detected as soon as the fabric is entered in the second dye-bath. The reason seems to be that cotton takes up more tannin when subjected to pressure than without; and this pressure is caused in part by the weight of the fabric itself and partly by the practice of weighting the goods down in the bath with wood in order to keep them submerged. In the author's view, it would be highly desirable to apply the tannin by padding. The dyeing-out with basic dyestuffs should be carried on in the cold, and as quickly as possible in order to afford the silk but little time to absorb the dyestuff. Concentrated bath liquors have been recommended for the same reason; but the author does not advise this, being of opinion that, under these conditions, the silk is liable to absorb a considerable amount of dye. Even in the cold bath, the silk always takes up some, and thus easily becomes darker than the cotton; but this is unimportant where the cotton does not appear on the same side of the fabric as the silk.

According to another two-bath recipe, the silk in the fabric is dyed in a slightly acid bath with distributable acid dyestuffs, as just described, and, after rinsing, the cotton is dyed with a substantive dyestuff in a cold or lukewarm, neutral, Glauber salt bath, under which conditions the silk is left intact.

Frequently, the serial order of these operations is reversed in practice, the cotton being dyed with a substantive dyestuff in a Glauber salt bath containing soap, which only imparts a slight coloration, if any, to the silk, the latter being then dyed with acid dyestuffs in a slightly acid bath, or with basic dyestuffs in a neutral, water bath. Of course, the substantive dyestuff must be one that will stand topping in an acid bath, in which case the cotton, as well as the silk, will take up dye from the second bath.

Finally, the silk may be dyed first with a basic dyestuff, as in the second method, and the cotton with a substantive dyestuff in a cold, neutral, Glauber salt bath.

Of the foregoing methods, the first and the last are the most widely practised, though the single-bath method is preferred wherever possible, the other being only used for such shades as cannot at present be obtained in a single bath.

Dichroic Effects on Half-Silk

There is no difficulty in obtaining dichroic effects on half-silk in great variety, the following methods, *inter alia*, being employed—

I. The silk is dyed, at 70–90° C., in an acid bath, with such wool dyes as do not draw on cotton, and, after rinsing, the cotton is mordanted, in a cold bath, with tannin and tartar emetic (as described in the previous section) and dyed with basic dyestuffs. To increase the brightness of the effect, it is advisable to use more tannin (up to 8 %), so that a large amount of dye will be fixed on the cotton. This latter must be dyed in the cold, and in presence of a little acetic acid, because basic dyestuffs draw on to the silk as well at higher temperatures. The dye-bath for the silk may contain sulphuric acid or formic acid, the silk being dyed, for instance, with brilliant croceine 3B, and the cotton with brilliant green.

II. The silk is dyed as above, rinsed, and the cotton dyed with substantive dyestuffs in presence of soap and soda, at as low a temperature as possible. Example: silk with orange II, and cotton with benzo pure blue.

III. The cotton is dyed with substantive dyestuffs which leave the silk white, or nearly so, in a bath containing soda and soap, the silk being then dyed, in a lukewarm bath containing acetic acid, with acid dyestuffs which have a minimum effect on cotton. Example:

cotton with benzo fast pink 2B1; silk with alkali fast green 3B.

IV. A single bath containing Glauber salt, soap and soda is used, the cotton being dyed with substantive dyestuffs inert towards silk (*e. g.* direct yellow R), and the silk with wool dyestuffs which draw in a neutral bath and leave the cotton untouched, or nearly so (*e. g.* acid violet 6BNB).

V. The cotton is dyed with diazo dyestuffs having little effect on silk (*e. g.* diazo black BHN), and after developing and rinsing, the silk is topped with acid dyestuffs, such as alkali fast green 3G.

VI. The cotton is dyed with sulphur dyestuffs, with addition of casein, in order to keep the silk perfectly white; and, after rinsing, the silk is dyed, as cold as possible, with acid or substantive dyestuffs in presence of acetic acid.

Black on Half-Silk

Black is one of the most difficult dyeings to produce on half-silk, and is still largely obtained by the old cutch process. According to Alexander, the fabric is first mordanted for two hours at 50° C. with copper sulphate and ferrous sulphate in a cutch bath, and is then dyed with logwood, fustic and 15 % of soap. To obtain a blue-black the fabric must first be blued. The only difficulty is to get an equal depth of colour on the two fibres, and the alumina lake of logwood has been successfully used for this purpose. The goods are entered in a cold bath of 10 % of indigo substitute, 5 % of indigo extract and 2½ % of alum, slowly raised to 60° C. and kept thereat for half-an-hour, 5 % of carbonate of soda being then added and the treatment continued for another half-hour. After rinsing, the fabric is treated in a bath of 30 % of cutch and 2 % of copper sulphate, for an hour at 38° C. and left to stand for several hours. This is succeeded by a bath of iron pyrolignite (4° Bé.), rinsing, and returning to the old cutch bath for an hour, finally dyeing with logwood (with or without fustic) and 15 % of soap.

The attempts to produce a real aniline black on half-silk encountered difficulties at first; but these have been overcome, and now the method is fairly common, though confined to large dye-works equipped with suitable apparatus. Nevertheless, it is always difficult to dye aniline black on such a susceptible material as half-silk, which requires careful handling of the kind best secured by selecting a dyeing process that weakens the silk as little as possible. The only one that fulfils this requirement is the oxidation black method. Experience has shown that the bath must be prepared in such a way as to liberate a minimum quantity of acid, which would render the silk brittle, and that a pure white aniline salt, free from any green or greyish-green tinge, should be chosen. A thickening agent to protect the silk from the destructive action of the acid, has also been found desirable.

A detailed description of the numerous modifications of the aniline black method is outside the scope of the present work; and it will be sufficient to give two of them, which have, moreover, been described in the works of Noelting & Lehne, Steinbeck and Silbermann.

One thousand parts of aniline hydrochloride and 250 of ammonium chloride (sal ammoniac) are dissolved in 4000 of hot water, and a solution is also made of 130 parts of copper sulphate and 400 of sodium chlorate in 4000 of water. When cold, these two solutions are mixed together and with a cold solution of 100 parts of wheaten starch, 100 of dextrin and 3 of sodium acetate in 5000 parts of water. Just before use, a solution of 0·5 part of ammonium vanadate in 60 of water is added. The half-silk is padded 2–3 times on the machine, under suitable pressure, being then dried at 30–40° C. and hung in the oxidation chamber, which is almost saturated with moisture for twelve hours. After being washed in a bath containing a small quantity of soda, the fabric is treated for a quarter of an hour, at 50–60° C., in the oxidation bath, washed, soaped at 60–70° C., and, if necessary, shaded with logwood or methylene blue.

In the copper sulphide process, the half-silk is padded with the following solution: 85 parts of aniline salt and 13 of wheaten starch dissolved in 400 of hot water and mixed with a solution of 17 parts of sodium chlorate and 2 of sal ammoniac, in 400 of water, 17 parts of copper sulphide, in the form of 30 % paste, being stirred in, and the whole made up to measure 1000 parts of water. The copper sulphide may be replaced by copper sulphocyanide, of which about 15 parts per 1000 of bath are taken. After oxidation the fabric is thoroughly washed in a bath of warm soda (35° C.), to eliminate the acid, starch, etc., and is then re-oxidised, for an hour, in a bath containing 3 % of chromate of potash and 0·5 % of sulphuric acid, at 80° C. Finally, it is soaped for an hour at 60–70° C., and shaded with methyl violet if necessary.

Diazo black is frequently used in place of oxidation black, such dyestuffs as diaminogene, Zambesi black and diazo fast black being taken. This method has the undoubted advantage of not weakening the fibre. The fabric is dyed with Glauber salt and soda (bath ratio 1 : 15), 8 % of dyestuff, 20–40 % of Glauber salt and 2–4 % of soda being used in the first bath. Umbrella fabrics are dyed on the jigger, in which case the bath liquor may be considerably stronger (1 : 10 to 1 : 8). Owing to the necessity for using fairly concentrated baths, it is desirable to use the old ones as many times as possible, in order to prevent waste. The amount of dyestuff required to replenish the bath must be ascertained in each case by experiment, but, on the average, the original amount of dyestuff can be reduced by one-fourth in the second and third baths, and by one-third in the fourth. It is highly advisable to leave the goods to draw for a long time in the cooling bath, after which they are rinsed and shaded. Diazotisation is effected in the usual manner, the following developers being recommended: for deep black, toluylenediamine chloride (developer H); for blue-black, B-naphthol (developer A). For intermediate gradations of black, the two developers may be combined, but the B-naphthol must largely predominate; for example, 8–9 parts to 1 of toluylenediamine. For black with a greenish tinge, resorcine may be added to the diamine to the extent of 50 % of the latter. After developing, the fabric must be well rinsed, because otherwise any residual diamine will set up an unpleasant brown tinge in the black when the goods are stored. Wooden vats are the best for diazotising and developing.

Dyeing Silk-Wool-Cotton Fabrics

Fabrics containing all three fibres are occasionally met with in commerce, either in the form of wool-cotton fabrics with fancy silk threads, or of wool-silk with fancy threads of flax or ramie. When such fabrics are to be dyed all one colour, this can be done with substantive dyestuffs and wool dyestuffs that draw in a neutral bath, as described in connection with wool-silk. If, on the other hand, polychrome—possibly three-colour—effects are to be produced, the matter becomes highly complicated. The thing is quite practicable, but it is doubtful whether the results obtained in this way are worth the trouble involved, since such three-colour effects can never compete with those obtained by weaving with coloured yarns. The process is well enough for demonstration purposes, but is more of the character of a toy.

Mechanical Operations in Half-Silk Dyeing

Since half-silk is only dyed in the piece, the jigger or reel vat alone come under consideration. The construction and operation of the jigger may be taken as known, and also that it is a favourite practice to connect several jiggers in series and work them together. For dyeing half-silk, the double jigger already described is still better. Both these machines, however, are less advisable in the case of half-silk fabrics that are closely woven and therefore difficult to dye through. Whilst they are well adapted for dyeing the silk, and also for mordanting the cotton with tannin and bottoming it with substantive dyestuffs, the reel vat is preferable for the actual dyeing process. On the jigger the goods are treated in the wide open condition, but with the reel they are twisted to form a rope; and the reel can be worked by hand instead of power. The reel is mounted on a sliding frame above the vat, and is wide enough to take two ropes of fabric. The ends of the pieces are sewn together, to form an endless rope. It is unnecessary to go into further details of manipulation. Stiff-edged ribbons and half-silk plush fabrics are also dyed on the reel, but care must be taken to keep them wide open and prevent any warping and consequent creases—for which purpose several specially designed machines are available. After dyeing, the goods are rinsed in the vat, drained in the hydro-extractor and dried, usually by hanging in a heated chamber. In large dye works, drying machines are also used, either the same as already described for dressing and drying silk, or a stenting and drying machine.

Drying is succeeded by a special cleaning process, performed by hand, the fabric being unwound from a roll and stretched over a table with a slightly arched top, on which it is well rubbed lengthwise with a clean rag or pad slightly moistened with a mixture of benzine and olive oil or paraffin, an excess being injurious. The benzine removes dirt, specks, etc., whilst the oil improves the lustre of the fabric. This treatment is used more particularly for dark colours, and always for black.

CHAPTER V

ARTIFICIAL SILK

Commercial Grades of Artificial Silk and their Properties

It was stated in the Introduction that artificial silk is not an artificially prepared silk, but a flexible, colourless filament, with vitreous lustre, that is made by forcing certain viscous compositions through fine nozzles. Considered solely from the point of lustre, this article may well be classed as a silk substitute; but it cannot compete with silk so far as its other properties are concerned. The history of this peculiar textile fibre dates back to the 'eighties, the first artificial silk, and fabrics woven therefrom, having been shown at the Paris International Exhibition of 1889. The inventor, Count de Chardonnet, a Frenchman, soon found imitators, all of whom used the same initial material, namely nitrocellulose. The first artificial silk was pure nitrocellulose, and was therefore too highly inflammable for practical use. By partial denitration (according to other reports, by treatment with ammonium phosphate) there finally resulted the product which is still known as Chardonnet silk. To the same category belong the artificial silks of Vivier, Lehner and the Tubize works; all four being also known as collodion silk, from the circumstance that the nitrocellulose is dissolved in ether-alcohol, the viscous solution (collodion) being forced through capillary tubes, the extruded filaments hardened in water and then wound on reels. This silk is prepared in a number of French, German and Belgian factories.

Another type of artificial silk is made by dissolving cellulose in ammoniacal copper oxide and extruding the solution. This variety, which is associated with the names of Fremery, Pauly, Langhans, Depaissis and others, is quite different, chemically, from Chardonnet silk, being pure cellulose. It is manufactured in Aachen and Elberfeld.

A third commercial variety, Viscose silk, is prepared from viscose—a product of the action of liquid carbon disulphide on cotton soaked in caustic soda; or, according to Acroyd and Krais, of the action of carbon disulphide vapour on mercerised cotton. It is the result of the researches of Cross and Bevan, and Stearn, and is manufactured, at Stettin, under the patents of Henckel von Donnersmarck.

Acetate Silk, the acetic ester of cellulose, is not yet on the market in the form of artificial silk.

The three commercial varieties of artificial silk are nearly alike in external appearance and are equal in point of lustre, which is really superior to that of natural silk. Against this undoubted advantage, however, must be set the serious drawback of considerably higher specific gravity. The filaments being manufactured by the extrusion of viscous liquids through fine capillary nozzles and having to be hardened afterwards, are not fibres in the usual sense of the word, but hardened masses shaped into filament form, and therefore structureless, their shape being lost when the constituent material softens again. This happens when artificial silk threads are immersed in hot water, as in the dyeing process. In fact, artificial silk softens in dyeing, becomes ductile and can be pulled apart and ruptured—a very objectionable quality, and one that entails the greatest care on the part of the dyer. In this respect, Chardonnet silk is the worst, since it softens at 35° C., whereas the other two do not become soft below about 60° C., and are therefore less difficult to handle in dyeing.

Chardonnet silk is liable to stretch under its own weight when the hank is in the dye-bath. Consequently, anything that tends to stretch it must be avoided, and it must be turned over and worked about as gently as possible, never forgetting that the material is devoid of structure and is merely a soft, ductile mass artificially brought into the shape of a filament.

Even when moistened, artificial silk becomes semi-translucent; and cellulose silk and viscose silk exhibit a faint violet coloration or fluorescence when mordanted with tannin. Artificial silk will not stand wringing, stretching or smoothing so long as it is wet; but when dry again, its former strength is regained, unless it has been permanently injured by treatment with acids or alkalis at an unduly high temperature.

Dyeing Artificial Silk

In order to enable the behaviour of artificial silk towards dyestuffs to be correctly appreciated, it must be borne in mind that all varieties, no matter how prepared, are derivatives of cellulose (that is to say, of cotton), and that they cannot dissociate themselves from their inherent characteristics as such. This explains why all attempts to dye artificial silks in the same way as natural silk, with acid dyestuffs in a boiling-hot bath of bast soap and sulphuric acid, necessarily failed, artificial silk not being silk at all. On the other hand, any dyestuff that will dye cotton will also dye artificial silk, and any method that will suit cotton is also applicable to artificial silk—of course with the limitation imposed by the fatal softening of artificial silk in hot dye-baths.

The various kinds of artificial silk do not all behave alike in respect of dyestuffs; a circumstance readily accounted for by their different chemical composition. Cellulose silk and viscose silk, although not chemically identical, behave very nearly alike towards dyestuffs and the dyeing process. Chardonnet silk also exhibits almost the same properties, except in the case of basic dyestuffs, which dye it direct, in the same way as silk; but not the other two. This behaviour towards basic dyestuffs, and the fact that it softens at as low a temperature as 35° C., afford a ready and reliable test for Chardonnet silk. The direct dyeings it gives, though not particularly intensive, are passable; and they can be considerably improved by mordanting the silk with tannin and tartar emetic. With the other two varieties this mordanting is essential for basic dyestuffs, as otherwise no absorption of the dye takes place.

Towards all other classes of dyestuffs, the three varieties of artificial silk behave exactly or approximately alike.

Substantive Dyestuffs are excellently adapted for all.

Sulphur Dyes give very handsome, bright colours, but are liable to produce bronzing and over-dyeing.

Vat Dyestuffs can also be successfully used, as also certain of the Acid and Sulphone Dyestuffs, the last two, however, only on Chardonnet silk.

In practice, the dyeing of artificial silk is carried on in the following manner.

Basic Dyestuffs.—The dyestuffs are dissolved, with the requisite degree of care, in water containing a little acetic acid, and the solution is added to the bath in small portions at a time, in order that the absorption may proceed gradually and uniformly. For Chardonnet silk, the bath must not be hotter than 35° C. (or 45° at the most), and no previous mordanting is needed. As already stated, however, the colours are not very full, and far darker shades can be obtained by mordanting the silk beforehand with tannin and tartar emetic in the same way as for natural silk. At the same time, the fastness to washing, friction and light is considerably increased, and a similar effect, as regards fastness to washing and the action of water, can be obtained by mordanting the dyed Chardonnet silk with 2 % of tannin and 1 % of tartar emetic.

Cellulose silk and viscose silk must be mordanted with these agents before dyeing. In this case, the dye-bath can be raised to 60° C., though this is not essential, the dyestuff being absorbed even in the cold. It should be noted that the darker shades obtained with basic dyestuffs have a great tendency to bronze, so that the dyestuff must be added with care and excessive temperatures avoided.

Substantive Dyestuffs are applied in a neutral Glauber salt bath (10–40 % according to the quantity of dyestuff), with an addition of 1 % of soda if the water is hard. The silk is entered at 30° C., and the bath slowly warmed—to 35° (40° at most) for Chardonnet silk, and to 60–65° C. for the other two. Dyeing takes one-half to one hour according to the depth required. For very deep shades on cellulose silk or viscose silk, the temperature may even be raised to 80° C. if necessary, or Glauber salt may be added to facilitate more complete absorption. In the case of dyestuffs that distribute with difficulty, 1–2 % of soap is added.

Diazo Dyestuffs are applied in the same way as the substantive dyestuffs, the material being then rinsed, diazotised and developed as for natural silk (*q. v.*).

Sulphur Dyes are used in the same way as for cotton. The bath is set in the usual way, but omitting the sodium lactate, raised to the boil, and cooled: to 80° C. for cellulose silk and viscose silk, and to 45° C. for Chardonnet silk, the bath being allowed to cool down further in dyeing.

Vat Dyestuffs are used in the same way as for real silk. All members of the group are suitable for cellulose silk and viscose silk, but Chardonnet silk is restricted to such as will dye in the cold. All the dyeings are fast in all respects.

Acid and Sulphone Dyestuffs are inapplicable to cellulose silk and viscose silk; and only about a dozen or so can be used on Chardonnet silk, namely those which dye in a neutral bath, such as fast red A, alkali blue and sulphonecyanine. The dyeings, however, are of no practical interest.

FABRICS WITH FANCY THREADS OF ARTIFICIAL SILK

For these new fabrics, the Farbenfabriken Bayer give the following dyeing recipes:—

Woollens with Fancy Threads of Cellulose—or Viscose Silk.—I. The wool is first dyed in a slowly-boiling bath, with addition of 10–15 % of Glauber salt and 3–5 % of formic acid or sulphuric acid, then thoroughly washed, and the artificial silk dyed in a cold bath with benzidine dyestuffs, 20–40 % of Glauber salt and ½ % of soda being added. If the silk appears too light, the temperature is carefully raised to 30–40° C.

II. The wool is dyed as in I, mordanted with tannin and tartar emetic, rinsed, and the artificial silk dyed with basic dyestuffs in a cold bath containing acetic acid.

III. The fabric is dyed with benzidine or other wool dyes that draw in a neutral bath, with addition of 20–30 % of Glauber salt, and, if necessary, 1–2 % of acetic acid. The goods are entered at 40–50° C., the bath being slowly warmed, and boiled for a short time as required. If the wool is too light, boiling is prolonged, or more dyestuff (or a little acetic acid) is added.

Cotton Fabrics with Fancy Threads of Artificial Silk.—The dye-bath contains 15 % of Glauber salt, 2 % of Marseilles soap and ½ % of soda, the fabric being entered at 30–40° C., and after treating for some time at this temperature, the bath is slowly warmed to 50–70° C., according to the depth of colour required, until the cotton is sufficiently covered. With larger quantities of Glauber salt and higher temperatures, the artificial silk will take up more dye than the cotton. To prevent this, it is advisable to take samples from time to time and, if the silk has the same depth as the cotton, allow the temperature to fall. A handsome deep black is obtained by diazotising and developing. For full shades a concentrated bath is necessary.

Half-Wool Fabrics with Artificial Silk Fancy Threads.—I. The wool is dyed in a slowly-boiling bath containing 10–15 % of Glauber salt and 3–4 % of formic acid or sulphuric acid. After a thorough rinsing, the cotton and artificial silk are dyed in a fresh, cold bath with benzidine dyestuffs, 20–50 % of Glauber salt and ½–1 % of soda. If the artificial silk comes out too pale, the temperature is carefully raised to 30–40° C. Any acid wool dyestuffs can be used in the first stage.

II. The wool is dyed as above, rinsed, mordanted with tannin and tartar emetic, and the cotton and artificial silk dyed with basic dyestuffs in a cold bath with addition of acetic acid.

III. The fabric is dyed with benzidine, or wool dyestuffs that dye in a neutral bath, with addition of 20–40 % of Glauber salt, entering and treating for half an hour at 50° C., then warming to about 90° C. and dyeing for half an hour longer. If the wool is not deep enough, a short boiling is given, or more wool dye is added.

INDEX

Absorbent properties of silk, 34, 35, 72–76
Acetate silk, 208
Acetic acid in dyeing, 50
Acid dye-stuffs, 77
—— dyeing with, 85–94
—— dyeing tussah with, 168
—— on half-silk, 192, 197
—— on wool-silk, 178–180, 183, 184
Acids, action of, on cotton, 189, 190
—— —— on silk, 35, 36, 189, 190
—— used in silk dyeing, 49–51
Alcohol for dissolving dyes, 62
Alkalis, action of, on cotton, 190
—— —— on silk, 36, 190
Alum in dyeing, 56
Alumina, mordanting with, 64, 65
Aluminium acetate in dyeing, 56
—— —— mordanting with, 66
—— nitro-acetate mordant, 57
—— sulphate in dyeing, 56
Amidodiphenylamine in diazotising, 100
Amidonaphtholsulphonic acid G. in diazotising, 100
Ammonia in dyeing, 52
Ammoniacal copper oxide, action of, on silk, 37
—— nickel oxide, action of, on silk, 37
Ammonium acetate as bast-soap substitute, 72
—— —— in dyeing, 52
—— sulphocyanide in dyeing, 52
—— —— in loading, 27
—— vanadate in dyeing, 60
Aqua regia, bleaching with, 15, 16, 17
—— in dyeing, 50
Artificial silk. *See* Silk, artificial
Azo dyestuffs, dyeing tussah with, 169

Basic dyestuffs, dyeing tussah with, 168
—— dyeing with, 80–85
—— on artificial silk, 210, 211
Basic dyestuffs on half-silk, 191, 192, 196, 197
—— on wool-silk, 177, 183, 184
Bast soap, 8
—— substitutes, 72
—— in dyeing, 68–72
Benzine for dissolving dyes, 62
Black, aniline, 131, 132
—— —— dyeing half-silk with, 202, 203
—— blue, 146
—— chestnut, 126
Black-dyeing silk, 117–132
Black dyeings on half-silk, 201–204
—— —— on silk, 93, 98, 102, 106, 117–132, 145, 146
—— —— on tussah, 168
—— English, 120
—— English, on Chappe silk, 130
—— for hat plush, 120
—— heavy, 127
—— heavy, with cutch and tin salt, 128
—— loaded cutch, 128
—— Lyons, 126
—— medium-weight cutch, 128
—— mineral, 127
—— mordant, 57
—— new blue-, 130
—— rapid, 120
—— souple, 127
—— velvet, 127
—— wool dyeings on wool-silk, 184
Bleaching half-silk, 188
—— silk, 10, 12–18
—— testing fastness to, 154
—— tussah silk, 162–165
—— wool-silk, 174
Blue dyeings on silk, 92, 97, 102, 106, 143
—— —— on wool silk, 184
—— navy, 143
Bluing in black-dyeing, 124–131
β-Naphthol in diazotising, 99
Borax in dyeing, 55
Bottoming with iron, 123–131
Bourette silk, dyeing, 146

Bran baths in dyeing, 63
Brightening silk after dyeing, 85, 154–156
Bronze dyeings, 146
Brown dyeings on silk, 93, 98, 102, 106, 141, 143
—— English, for souple silk, 141
—— tobacco, 143
Byssus silk, 2

Calcium acetate in dyeing, 55
Capillarity of silk, 137
Castor oil soap in dyeing, 61
Caustic soda in dyeing, 52
Cellulose silk, 208, 209, 210
Cerium salts, mordanting with, 67
Chappe silk, dyeing, 144–146
—— English black on, 130
—— mordanting, 144
Chardonnet silk, 207, 209, 210
Chemical composition of silk, 35
Chlorine, action of, on cotton, 190
—— —— of, on silk, 36, 190
Chrome alum in mordanting, 58
—— mordant, 58
Chromic chromate. *See* Chrome mordant
Chromium chloride in mordanting, 58
—— fluoride in mordanting, 58
—— salts, mordanting with, 66
Citric acid in dyeing, 51
Cochineal for dyeing silk, 116
Collodion silk, 207
Colour dyeing, 136–151
Conditioning silk, 34, 37
Copper acetate in dyeing, 60
—— salts, action of, on silk, 37, 38
—— —— in black-dyeing on half-silk, 202–203
—— sulphate in dyeing, 60
—— sulphide in dyeing, 60
Coppering, 84
Cotton, action of acids on, 189, 190
—— —— of alkalis on, 190
—— —— of chlorine and hypochlorites on, 190
—— —— of, on metallic salts, 191
Cottons with fancy threads of artificial silk, 213
Count of silk, 39
Crabbing wool-silk, 171
Cuite silk, 6
—— bleaching, 14, 15
—— loading, 29
Cutch, dyeing with, 123–131
—— loading with, 22, 23, 24

Developers in diazotising, 100, 101
Diazo dyestuffs on artificial silk, 211
—— on half-silk, 197, 203, 204
Diazotised dyestuffs, dyeing with, 98–102
Diazotising, 98–101
Dichroic effects on half-silk, 200, 201
—— —— on wool-silk, 182–185
Drying silk, 40
Dye bath, preparing, 78, 79, 86, 89, 95, 96, 103, 111, 112, 119, 178, 179, 180, 193, 194, 198
Dye-bath temperatures, 83, 86, 89, 95, 96, 103, 109, 113, 119, 120, 121, 124, 128, 132, 167, 178, 179, 180, 183, 194, 213, 214
Dyeing artificial silk, 209–214
—— black, 117–132
—— bourette silk, 146
—— chappe silk, 144–146
—— combination, 83, 84, 85, 90, 137, 139
—— dry, 148
—— half-silk, 191 206
—— machinery and appliances, 41–43
—— silk, 80–151
—— —— in the piece, 148, 149
—— silk-wool-cotton fabrics, 204
—— single-bath, 107
—— special effects in, 146–148
—— treatment of silk after, 154–156
—— tussah silk, 165–169
—— wool-silk, 177–185
—— with acid dyestuffs, 85–94
—— with basic dyestuffs, 80–85
—— with cutch, 123–131
—— with diazotised dyestuffs, 98–102
—— with katigene dyestuffs, 109–110
—— with mordant dyestuffs, 102–108
—— with natural dyestuffs, 115–116
—— with substantive dyestuffs, 94–98
—— with sulphone dyestuffs, 102
—— with sulphur dyestuffs, 108–110
—— with tannins and iron salts, 121–128
—— with vat dyestuffs, 110–115
Dyestuffs, acid, on half-silk, 192, 197
—— —— on tussah, 168
—— —— on wool-silk, 178–180, 183, 184
—— azo, on tussah, 169
—— basic, on artificial silk, 210, 211

Dyestuffs, basic, on half-silk, 191, 192, 196, 197
—— —— on tussah, 168
—— —— on wool-silk, 177, 183, 184
—— behaviour of silk towards, 72–76
—— classification of, 75
—— diazo, on artificial silk, 211
—— —— on half-silk, 197, 203, 204
—— distributing, 88, 89
—— non-distributing, 88, 89
—— mordant, on half-silk, 192
—— —— on wool-silk, 181
—— selecting, 76–78
—— substantive, on artificial silk, 211
—— —— on half-silk, 192
—— —— on tussah, 168
—— —— on wool-silk, 180, 181
—— sulphone, on wool-silk, 181
—— sulphur, on artificial silk, 212
—— —— on half-silk, 192, 198
—— vat, on artificial silk, 212
—— —— on half-silk, 193, 198

Écru silk, 6, 12
—— bleaching, 15
Electrical properties of silk, 34
Ethyl-β-naphthylamine in diazotising, 100

Fabrics with fancy threads of artificial silk, 212–214
Fastness to acid, 153
—— to alkali, 153
—— to bleaching, 154
—— to boiling, 153
—— to light, 153
—— to light, improving, 84
—— to milling, 152
—— to soap, 152
—— to sulphur, 154
—— to topping, 153
—— to water, 151
—— to water, improving, 84, 91
Ferric nitro-acetate in dyeing, 58
—— sulphate mordant, 57
Ferrous sulphate in dyeing, 58
—— pyrolignite in mordanting, 57
Fibroin, 5, 30–32
Flock silk, 4
Fluorescent dyeings, 146
Formaldehyde in dyeing, 63
Formic acid in dyeing, 50
Froth dyeing method of scouring silk, 9
Fuchsine, dyeing with, 81, 82, 83
Fustic for shading logwood black, 115

Gallnut extract, loading with, 21
—— dyeing with, 121, 122
Gassing silk goods, 41
—— half-silk, 186
—— wool-silk, 171
Gilding silk, 157
Glauber salt in dyeing, 54
Gloria fabrics, 2
Glue in tannin loading, 63
Glycerine for dissolving dyes, 63
Green dyeings on silk, 92, 97, 102, 105, 116, 142
—— —— on wool-silk, 184
—— Russian, 142
—— umbrella, 143
Grége, 4
Grey, Carmelite, 142
Greys, dyeing, 140

Half-silk, 3
—— black on, 201–204
—— dichroic effects on, 200, 201
—— dyeing, 191–206
—— —— mechanical operations in, 205–206
—— fabrics, 186–206
—— preliminary treament, 186–188
—— properties and behaviour towards dyestuffs, 188–193
—— shading with basic dyestuffs, 196
Half-wool fabrics with artificial silk fancy threads, 213, 214
Hard silk, bleaching, 15
—— loading, 30. *See also* Écru
Hydrochloric acid in dyeing, 50
Hydrogen peroxide, bleaching with, 17, 18, 62, 162
Hypochlorites, action of, on cotton, 190
—— —— on silk, 190

Iron bottoming, 123–131
——loading, 29
—— salts, loading and dyeing with, 121–131
—— —— mordanting with, 67

Jaspures, 148

Katigene black, 110
—— dyeings, coloured, 110
—— dyestuffs, dyeing silk with, 109, 110
Killing yellow tinge in white silk, 138

Lead acetate in loading, 60
Lime in dyeing, 52

Loading silk, 13, 14, 18–30
—— mixed, 23
—— tests for, 133–136
—— tussah silk, 165
—— with tannins and iron salts, 121–128
Logwood, black dyeing with, 117–121
—— for dyeing and loading silk, 115
Lustring silk, 40

Magnesium sulphate in loading, 56
Marseilles soap in dyeing, 61
Matching colours, 104, 149–151
Mechanical treatment of silk before dyeing, 39–41
Metallic salts, action of, on silk, 36, 37, 38
Meta-toluylenediamine hydrochloride in diazotising, 100
Mi-cuite, silk, 7
Mode colours, dyeing, 140
Mordant dyestuffs, 77
—— —— dyeing with, 102–108
—— —— on half-silk, 192
—— —— on wool-silk, 181
Mordanting artificial silk, 211
—— chappe silk, 144
—— in black dyeing, 119, 120, 126, 127, 128, 129
—— silk, 63–68
—— wool-silk, 181
Mulberry silk, 2
Mussel silk, 2

Natural dyestuffs, dyeing silk with, 115, 116
Nitrate mordant, 57
Nitric acid in dyeing, 50
Nitrosulphuric acid, bleaching with, 17

Olein soap in dyeing, 61
Ombres, 147
Orange dyeings on silk, 92, 97, 101, 105
Orchil for dyeing silk, 115
Organzine, 4
Oxalic acid in dyeing, 51
Oxidation of vat dyestuffs, 114

Permutite method of softening water, 45–49
Phenol in diazotising, 100
Phosphate-silicate loading, 28
Piece dyeing, 148, 149
Pink salt, 23
—— loading with, 59, 128, 129
Porosity of silk, 34
Potassium-antimony tartrate. *See* Tartar emetic
Potassium chlorate in dyeing, 53
—— chromate in dyeing, 53
—— ferrocyanide in dyeing, 53
—— permanganate, bleaching with, 53, 164
—— tartrate in dyeing, 53

Raw silk, 4, 6
—— dyeing black, 121
—— loading, 30
Reddish-brown mordant, 57
Red dyeings on silk, 91, 97, 101, 104, 116
—— —— on wool-silk, 184
Reeling silk, 4
Resorcine in diazotising, 100

Sericin, 5, 6, 7, 8, 30–32
Scouring half-silk, 186–188
—— silk, 5–9
—— tussah silk, 161
—— wool-silk, 172, 173
Scroop, 32, 33
—— imparting, 155
Shot effects, 147
—— —— on wool-silk, 183, 184
Silk, absorption of dyestuffs by, 191, 192
—— absorption of tannins by, 191
—— action of acids on, 189, 190
—— —— of alkalis on, 190
—— —— of chlorine and hypochlorites on, 190
—— —— of, on metallic salts, 191
—— artificial, 2, 207–214
—— —— commercial grades and properties, 207–209
—— —— dyeing, 209–214
—— —— fancy threads in fabrics, 212–214
—— —— mordanting, 211
—— bleaching, 10, 12–18
—— properties of, 30–38
Silk-wool-cotton fabrics, dyeing, 204
Smoothing silk, 40
Soap, action of, on silk, 36
—— baths for scouring half-silk, 186–188
—— —— in dyeing half-silk, 194
—— —— in dyeing tussah, 166, 167
—— —— in silk scouring, 7–9
—— in dyeing, 60–62, 68–72
Sodium acetate in dyeing, 55
—— bicarbonate in dyeing, 54
—— bisulphite in dyeing, 54

Sodium β-naphthol in diazotising, 100
—— carbonate in diazotising, 101
—— —— in dyeing, 53
—— chloride in dyeing, 54
—— hydrosulphite, bleaching with, 16
—— —— in dyeing, 54
—— hydroxide. *See* Caustic soda
—— lactate in dyeing, 55
—— nitrate in dyeing, 55
—— perborate in dyeing, 55
—— peroxide, bleaching with, 18, 162, 163
—— —— in dyeing, 52
—— phosphate in loading, 26, 27, 28
—— silicate. *See* Water glass
—— sulphate. *See* Glauber salt
—— sulphide in dyeing, 55
—— tungstate in dyeing, 55
Softening silk after dyeing, 155
Soluble oils in dyeing, 62
Souple silk, 6, 9–12
—— bleaching, 15
—— loading, 30
Soupling silk, 9–12
Specific gravity of silk, 34
Spun silk, bleaching, 18
Stannic chloride in loading, 23, 24, 25, 26, 28, 59
Stannous chloride in dyeing, 59
Stretching silk, 40
Structure of silk, 33
Substantive dyestuffs, 77
—— —— dyeing tussah with, 168
—— —— dyeing with, 94–98
—— —— on artificial silk, 211
—— —— on half-silk, 192
—— —— on wool-silk, 180, 181
Sugar, loading with, 20, 21
Sulphone, dyestuffs, dyeing with, 102
—— —— on wool-silk, 181
Sulphur, bleaching with, 14, 15
Sulphur dyes, 78
—— dyestuffs, dyeing silk with, 108–110
—— —— on artificial silk, 212
—— —— on half-silk, 192, 198
Sulphuric acid in bleaching, 15
—— in dyeing, 49
Sulphurous acid, bleaching with, 15, 16, 49
Sumach, loading with, 21, 22, 23

Tannic acid in dyeing, 51
Tannin in dyeing, 51
—— loading with, 21–24
Tanning, after-, 156
Tannins, absorption of, by silk, 191
—— loading and dyeing with, 121–128
—— mordanting with, 67, 68
Tartar emetic in dyeing, 60
Tartaric acid in dyeing, 51
Tensile strength of silk, 33
Testing dyed silk for loading, 133–136
—— silk dyeings for fastness, 151–154
Thiourea in loading, 27
Thorium waste for loading silk, 29
Tin acetate in dyeing, 59
—— ammonio-chloride. *See* Pink salt
—— loading, 24
—— phosphate, loading with, 25–28, 129
—— salt. *See* Stannous chloride
—— salts, mordanting with, 67
Titre of silk, 33, 39
Turkey-red oil in dyeing, 61, 62
Turmeric for dyeing silk, 116
Tussah silk, 2, 158–169
—— bleaching, 18, 162–165
—— dyeing, 165–169
—— loading, 165
—— properties, 158–160
—— scouring, 161
Two-colour dyeings, 147
—— effects. *See also* Dichroic effects

Value of silk, estimating, 38
Vanadium chloride in dyeing, 60
Vat dyestuffs, 78
—— —— dyeing silk with, 110–115
—— —— on artificial silk, 212
—— —— on half-silk, 193, 198
Violet dyeings on silk, 93, 98, 102, 106
—— —— on wool-silk, 184
Viscose silk, 208, 209, 210

Watered effects, 148
Water-glass in dyeing, 55
—— loading with, 28
Water in silk dyeing, 43–49
—— removing iron from, 48
—— softening, 43–49
Weld for dyeing silk, 116
White silk, killing yellow tinge in, 138
Woollens with fancy threads of artificial silk, 212, 213
Wool-silk, 3, 170–185
—— bleaching, 174

Wool-silk crabbing, 171
—— dichroic effects on, 182–185
—— dyeing, 177–185
—— gassing, 171
—— mordanting, 181
—— properties and behaviour towards dyestuffs, 174–177
—— scouring, 172, 173
—— steaming, 172
—— treatment before dyeing, 170–177

Yellow dyeings on silk, 92, 97, 102, 105, 116
—— —— on wool-silk, 184

Zeoliths in softening water, 46–49
Zinc-bisulphite vat, 114
Zinc chloride, action of, on silk, 37
—— dust in dyeing, 63
—— hydrosulphite in stripping dyes, 60
Zirconium salts for loading silk, 29

X
R19

SOUTHEASTERN MASSACHUSETTS UNIVERSITY
TP901.G3
Dyeing silk, mixed silk fabrics and arti
3 2922 00086 334 7

DATE DUE

CANCELLED
JUL 2 1979

AUG 1 3 1979

5/15/83

RETURNED
OCT 1989

IL: 580040
due: 4/12/91

UPI

Printed in USA

TP901
G3

TP901.G3